CARLSON ENVIRONMENTAL, INC.

Sent by Messenger

March 16, 1999

PN 9566C

Mr. John J. O'Grady
Remedial Project Manager
US EPA Region V
Superfund Division
77 West Jackson
Chicago, Illinois 606064

RE: Supplement to Laboratory Quality Assurance Program
Fansteel, Inc.
North Chicago, Illinois

Dear Mr. O'Grady:

The enclosed material is intended to supplement the *Quality Assurance Program* prepared by Great Lakes Analytical, the laboratory selected by Carlson Environmental, Inc. (CEI) to perform the laboratory analysis required in the proposed site investigation. Specifically, Great Lakes Analytical's *Quality Assurance Program* was submitted as Attachment D to CEI's *Site Investigation Work Plan*, dated April 1998.

The enclosed information supplements the *Quality Assurance Program*, addresses the pertinent comments in your response letter dated July 20, 1998, and includes laboratory Standard Operating Procedures (SOPs). CEI's revised *Quality Assurance Project Plan (QAPP)* is being submitted simultaneously, under separate cover.

Please feel free to contact Margaret Karolyi of CEI at (312) 704-8843 or Kevin Keeley of Great Lakes Analytical if you need any additional information.

Respectfully submitted,

CARLSON ENVIRONMENTAL, INC.

Margaret Karolyi

Margaret M. Karolyi, P.E.
Project Manager

enclosure

cc: Kevin Keeley, Great Lakes Analytical
Clifton A. Lake, McBride Baker & Coles
Jonathan E. Jackson, Fansteel, Inc.

ENCLOSURES

Great Lakes Analytical Response Letter

Addendum to Log-in Standard Operating Procedures

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Standard Operating Procedure for the Determination of Total Cyanide and Cyanide Amenable to Chlorination in Liquids and Solids

Standard Operating Procedure for the Digestion of Liquids for the Analysis of Metals

Standard Operating Procedure for the Digestion of Solids for the Analysis of Metals

Standard Operating Procedure for Analysis of Metals Using GFAA

Standard Operating Procedure for Analysis of Metals Using ICP

Standard Operating Procedure for Organic Extraction and Sample Preparation for Semivolatile Determinative Methods

Standard Operating Procedure for Polychlorinated Biphenyls by Gas Chromatography:

Capillary Column Method

Standard Operating Procedure for the Determination of Volatile Organic Compounds by Purge-and-Trap and Gas Chromatography Mass Spectrometry

Standard Operating Procedure for Polynuclear Aromatic Hydrocarbons by HPLC

Great Lakes Analytical Response Letter

GREAT LAKES ANALYTICAL

1380 Busch Parkway
Buffalo Grove Illinois 60089

Email info@glalabs.com
(847) 808-7766 FAX (847) 808-7772

October 29, 1998
Carlson Environmental, Inc.
Attn: Margaret Karolyi
312 West Randolph Street
Chicago, IL 60606

Dear Margaret:

Below are Great Lakes Analytical's responses to US EPA comments included in your August 17 transmittal:

50. Section 4.2, Item 1, Page 8: An SOP for the preparation of bottles for EPA Method 5035 is attached.

56. Section 5.2, Laboratory Equipment, Page17: Calibration procedures for the analytical methods are found in the included SOPs.

58. Section 7.0, ANALYTICAL SERVICES, Page 17-18: The following SOPs are enclosed:

- The Determination of Mercury in Liquids and Solids, GLA 245.1/5 BG, Rev 2.0
- The Determination of Total Cyanide and Cyanide Amenable to Chlorination in Liquids and Solids, GLA 335.4 BG, Rev. 2.0
- The Digestion of Liquids for the Analysis of Metals, GLA 3015 BG, Rev. 3.0
- The Digestion of Solids for Analysis of Metals, GLA 3050 BG, Rev. 3.0
- Analysis of Metals Using ICP, GLA 6010 BG, Rev. 2.0
- Analysis of Metals Using GFAA, GLA 7000 BG, Rev. 2.0
- Organic Extraction and Sample Preparation for Semivolatile Determinative Methods, GLA 3500 BG, Rev. 1.1
- Polychlorinated Biphenyls by Gas Chromatography: Capillary Column Method, GLA 8082 BG, Rev. 1.0
- The Determination of Volatile Organic Compounds by Purge and Trap and Gas Chromatography Mass Spectrometry GLA 8260 BG, Rev. 2.0
- Polynuclear Aromatic Hydrocarbons by HPLC, GLA 8310 BG, Rev. 1.1

59. Section 7.0, ANALYTICAL SERVICES, Page 17-18: Method performance studies for Tantalum will follow.

62. Section 8.2, Laboratory Quality Control Checks, Page 18-19: A description of corrective actions for laboratory out of control events can be found in Section 6.0 of the attached SOPs.

63. Section 8.2, Laboratory Quality Control Checks, Page 19, last bullet: Section 6.6 of Polychlorinated Biphenyls by Gas Chromatography: Capillary Column Method, GLA 8082 BG, Rev. 1.0 addresses confirmation procedures to be employed. As detailed in this section, the laboratory will report the higher of the two results when there is significant difference between the two measurements.

64. Section 9.1, Field Data, Page19: Not applicable to Great Lakes Analytical

65. Section 9.2, Laboratory Data, Page 20: Project Reporting Limits have been transmitted to C.I.

71. Section 5.1, Sample Containers and Preservation, Page1: Enclosed is a copy of our SOP for the Preparation of Sample Containers for EPA 5035.

72. Section 6.3, Sample Log-in, Page 12: Sample Chain of Custody will be maintained and documented prior to receipt at the laboratory. Great Lakes Analytical maintains a secure laboratory facility. Access is restricted and limited to employees and authorized visitors. Custody of samples within the laboratory is well documented in the log books, bench sheets and run logs maintained by our Chemists and Technicians.

73. Section 6.3, Sample Storage, Page 13: After sample log-in, samples for Volatile Organic analysis are stored in the Volatile Organics Department separate from samples for other types of analysis as well as standards and extracts.

74. Section 8.0, Analytical Quality Control, Page 15-23: A table listing MDLs, PQLs and RLs was transmitted previously. Tables with accuracy control limits and surrogate control limits are enclosed

Sincerely,
GREAT LAKES ANALYTICAL

Kevin W. Keeley
President Laboratory Director

Addendum to Log-in Standard Operating Procedures

GREAT LAKES ANALYTICAL

ADDENDUM TO THE LOG-IN STANDARD OPERATING PROCEDURES

STANDARD OPERATING PROCEDURE FOR THE PREPARATION OF SAMPLE CONTAINERS FOR EPA METHOD 5035

GLA 5035 BG

REVISION 1.0

Date Approved:

Department Manager: _____

QA QC Manager: _____

Laboratory Manager: _____

Bottle Preparation for Volatiles Method 5035

BOTTLE PREPARATION
FOR
VOLATILES METHOD 5035

The specific bottles supplied by the laboratory for the 5035 method depends on the expected concentration range of the sample. Separate bottles will be supplied for low concentration soil samples and high concentration soil and solid waste samples. The sample vials will be prepared in the laboratory and supplied to our customers.

Low Concentration Soil Samples

1. Add a clean magnetic stirring bar to each clean vial.
2. Add preservative to each vial. The preservative is of 1 gram of sodium bisulfate.
3. Add 5 ml of organic-free reagent water to each vial.
4. Seal the vial with the screw-cap and septum seal.
5. Affix a label to each vial.
6. Weigh the prepared vial to the nearest 0.01 gram, write the weight on the vial.
7. For low level analysis include two to three of these vials along with one methanol preserved container described below as well as a dry weight container.

High Concentration Soil Samples-Collected & Preserved in the Field

1. Add 25 ml of methanol to a clean vial. Label the vial appropriately with contents and date of preparation.
2. Affix a label to a 2 ounce container. Weigh the container to the nearest 0.01 grams. Write the weight on the label.
3. For high level analysis include one methanol vial and container as well as an additional jar for the dry weight determination.

Control Limits

CONTROL LIMITS

Analyte	Method	Matrix	Laboratory Control Sample	Matrix Spike Control Limit (%Rec.)	Matrix Spike Control Limit (%RPD)	Matrix Spike 2-Sigma (Warning) (%Rec.)	Matrix Spike 2-Sigma (Warning) (%RPD)
11 DCE	8260	Soil	80-120	54-132	25	67-119	20
Benzene	8260	Soil	80-120	88-124	9	88-124	7
TCE	8260	Soil	80-120	67-121	17	75-113	14
Toluene	8260	Soil	80-120	73-121	16	81-114	12
Chlorobenzene	8260	Soil	80-120	81-117	13	87-110	10
11 DCE	8260	H2O	80-120	56-128	21	68-115	16
Benzene	8260	H2O	80-120	68-128	16	79-118	12
TCE	8260	H2O	80-120	59-137	36	72-123	27
Toluene	8260	H2O	80-120	79-127	15	86-119	11
Chlorobenzene	8260	H2O	80-120	82-118	16	88-112	12
Vinyl Chloride	8260	TCLP	80-120	58-142	16	73-128	11
11 DCE	8260	TCLP	80-120	68-128	20	78-119	15
Chloroform	8260	TCLP	80-120	65-119	13	74-109	9
MEK	8260	TCLP	80-120	35-161	39	56-140	30
Carbon Tetrachloride	8260	TCLP	80-120	62-128	10	74-116	9
Benzene	8260	TCLP	80-120	82-112	9	87-107	7
12DCA	8260	TCLP	80-120	80-122	14	87-114	11
TCE	8260	TCLP	80-120	76-106	15	82-101	11
PCE	8260	TCLP	80-120	77-113	12	84-106	9
Chlorobenzene	8260	TCLP	80-120	84-108	12	89-104	8

Date Established: 10/28/97

To Be Revised: 10/28/98

Department Mgr.: Bridgid M. J. Howland

QA/QC Mgr.: Ron Osborn

Method Detection Limits, Practical Quantitation Limits, Reporting Limits, Control Limits - Organic

Method Detection Limits, Practical Quantitation Limits, Reporting Limits, Control Limits

Organic Analytes	Method	Water			Soil/Sediment			Control Limits			
		MDL mg/L	PQL mg/L	R.L. mg/L	MDL mg/kg	PQL mg/kg	R.L. mg/kg	Water LC	Water MS	Soil LCS	Soil MS
PCB 1016/1260	8082	N/A	N/A	N/A	3.5	11	50	28-124	28-124	25-174	25-167
Surrogates											
Decachlorobiphenyl	8082	N/A	N/A	N/A	N/A	N/A	N/A	25-154	25-154	25-160	25-160
Tetrachloro-m-xylene	8082	N/A	N/A	N/A	N/A	N/A	N/A	25-145	25-145	25-97	25-97
Naphthalene	8310	0.0161	0.051	3.0	1.66	5.3	8.7	46-106	46-106	61-111	64-116
Phenanthrene	8310	0.0196	0.062	0.30	1.7	5.4	8.7	42-122	42-122	62-124	62-128
Pyrene	8310	0.0206	0.066	1.0	1.3	4.0	8.7	49-119	49-119	59-110	38-140
Benzo(k)Fluoranthene	8310	0.0159	0.051	0.050	0.28	0.89	8.7	45-147	45-147	65-122	62-127
Indeno(1,2,3-cd)Pyrene	8310	0.0243	0.077	0.20	1.4	4.3	8.7	51-142	51-142	48-110	25-166
Surrogate											
7,12=Dimethylbenz(a)anthracene	8310	N/A	N/A	N/A	N/A	N/A	N/A	28-182	28-182	25-211	25-211

Method Detection Limits, Practical Quantitation Limits, Reporting Limits, Control Limits - Inorganic

Method Detection Limits, Practical Quantitation Limits, Reporting Limits, Control Limits

Inorganic Analytes		Water			Soil/Sediment						
ICP Metals		MDL mg/L	PQL mg/L	R.L. mg/L	MDL mg/kg	PQL mg/kg	R.L. mg/kg	Water LC	Water MS	Soil LCS	Soil MS
Aluminum	6010B	0.091	0.29	0.20	4.6	14	10	85-115	75-125	85-115	75-125
Antimony	6010B				1.1	3.5	5.0	85-115	75-125	85-115	75-125
Barium	6010B	0.00072	0.0023	0.50	0.036	0.11	25	85-115	75-125	78-110	43-127
Beryllium	6010B	0.00038	0.0012	0.0040	0.019	0.061	0.50	85-115	75-125	85-115	75-125
Cadmium	6010B	0.0041	0.013	0.0050	0.20	0.65	0.50	94-114	89-113	87-107	73-109
Calcium	6010B	0.072	0.23	0.20	3.6	11	10	85-115		85-115	75-125
Chromium	6010B	0.0061	0.019	0.010	0.31	0.97	0.50	94-114	87-111	86-106	67-111
Cobalt	6010B	0.0073	0.023	0.050	0.36	1.2	2.5	85-115		85-115	75-125
Copper	6010B	0.0013	0.0040	0.050	0.063	0.20	2.5	89-113	85-109	83-103	59-108
Iron	6010B	0.014	0.045	0.050	0.70	2.2	2.5	85-115	75-125	85-115	75-125
Lead	6010B				0.94	3.0	2.5			77-113	74-102
Magnesium	6010B	0.050	0.16	0.20	2.5	7.9	10	85-115	75-125	85-115	75-125
Manganese	6010B	0.0010	0.0031	0.050	0.048	0.15	2.5	85-115	75-125	85-115	75-125
Nickel	6010B	0.012	0.038	0.050	0.60	1.9	2.5	85-115	75-125	85-115	75-125
Potassium	6010B	0.050	0.16	0.20	2.5	7.9	10	85-115	75-125	85-115	75-125
Silver	6010B	0.0025	0.0080	0.050	0.13	0.40	2.5	83-111	1-133	77-101	24-116
Sodium	6010B	0.26	0.82	0.20	13	41	10	85-115	75-125	85-115	75-125
Thallium	6010B				1.2	3.7	1.6	85-115	75-125	85-115	75-125
Vanadium	6010B	0.0046	0.015	0.049	0.23	0.74	2.5	85-115	75-125	85-115	75-125
Zinc	6010B	0.0059	0.019	0.50	0.30	0.95	25	85-115	75-125	85-115	75-125
Furnace Metals											
Antimony	7041	0.0012	0.0030	0.006				85-115	75-125	85-115	75-125
Arsenic	7060	0.0013	0.0041	0.050	0.064	0.20	2.5	85-115	75-125	83-119	69-121
Lead	7421	0.00022	0.00069	0.0050	0.011	0.035	0.25	87-115	78-118		
Selenium	7740	0.0021	0.0066	0.010	0.10	0.33	0.50	85-115	75-125	77-117	68-116
Thallium	7841	0.00066	0.0021	0.0020				85-115	75-125	85-115	75-125
Other Inorganic Analytes											
Hg	7470	0.000038	0.00012	0.0020	0.0076	0.024	0.010	89-113	80-116	86-114	78-122
CN	9012	0.0014	0.0044	0.010	0.035	0.11	0.25	77-109	74-109	72-116	70-118

Standard Operating Procedure for the Determination of Mercury in Liquids and Solids

GREAT LAKES ANALYTICAL

STANDARD OPERATING PROCEDURE

FOR

THE DETERMINATION OF MERCURY IN

LIQUIDS AND SOLIDS

GLA 245.1/5 BG

Revision 2.0

Approved By

Department Manager: _____ Date 9/16/98

Quality Assurance Manager: _____ Date _____

Laboratory Director: _____ Date _____

1.0 APPLICABILITY

This standard procedure (SOP) provides instructions for the determination of mercury by cold-vapor atomic absorption spectrophotometry. This SOP is an interpretation of EPA Methods 245.1 and 245.5, *Standard Methods no.* 3112, *Section* B, *and methods* SW-846 *no's* 7470A *and* 7471A. This SOP is to be used in conjunction with the analysts' in-laboratory training, the Great Lakes Analytical Chemical Hygiene Plan (CHP), and the Great Lakes Analytical Quality Assurance Program.

1.1 MATRICES

This SOP may be used for aqueous, solid, and mixed samples, including soils, sediments, sludge, domestic and industrial wastes. Concentration range for samples is typically 0.2 to 2.5 ppb. Higher concentrations may be determined by sample dilution.

1.2 REGULATORY APPICABILITY

40 CFR 121

2.0 SUMMARY

Liquid samples are digested with nitric and sulfuric acids, potassium permanganate and potassium persulfate. Solid samples are digested with *aqua regia* (nitric and hydrochloric acids) and potassium permanganate. A series of standards is digested and analyzed concurrently to produce a calibration curve from which sample results are determined.

A semi-automatic cold-vapor apparatus is used to produce metallic mercury vapor from the resultant digestates. The sample is automatically mixed with hydrochloric acid and stannous chloride solution. The mercury is reduced to the elemental state which is then bubbled out of solution and carried into the instrumental light path by means of an inert argon gas flow. The atomic absorption of this vapor is read at 253.7 nm. Deuterium arc background correction is used to automatically correct for interference due to water vapor, chlorine, or other contaminants which absorb or block light at this wavelength. The absorption read by the spectrophotometer is proportional to the concentration of mercury in the original sample.

See Appendix A for method exceptions.

3.0 SAFETY

3.1 GENERAL

This SOP does not address all safety issues associated with its use. A reference file of material safety data sheets (MSDS's) is available to all personnel, along with the Great Lakes Analytical (GLA) Chemical Hygiene Plan.

The toxicity or carcinogenicity of each reagent used in this SOP has not been precisely determined, however, each chemical should be treated as a potential health hazard. Exposure to these chemicals should be reduced to the lowest possible level. Gloves are worn when handling chemicals and reagents.

3.2 CHEMICAL HYGIENE PLAN

The GLA Chemical Hygiene Plan (CHP) is designed to establish safe work procedures and minimize exposure to hazardous chemicals encountered in the laboratory. The CHP provides information to employees regarding potential hazards and training to minimize these hazards.

3.3 HAZARDOUS SAMPLES

All samples that are received by the laboratory have the possibility of containing hazardous pollutants. They should be treated with caution at all times Gloves are worn when handling samples. Also see the Great Lakes Analytical SOP for Hazardous Sample Management.

3.4 METHOD SPECIFIC CHEMICALS

Potassium permanganate and persulfate are strong oxidizers They can burn eyes and skin Also, they can cause a fire if mixed with incompatible chemicals

4.0 INTERFERENCES

4.1 Potassium permanganate is added to eliminate any possible interference from sulfide Concentrations as high as 20 mg/L of sulfide (as sodium sulfide) do not interfere

4.2 Concentrations of copper as high as 10 mg/L do not interfere Higher concentrations may cause interference.

4.3 Samples containing high levels of chlorides (such as sea water, brine, and industrial effluents) may require additional permanganate Chlorides are converted to free chlorine, which also absorbs at 253 nm. Chlorine is eliminated before the reduction of mercury by using an excess of hydroxylamine reagent.

4.4 Certain volatile organic materials that absorb in the 253 nm region may also cause interference. A preliminary run without reagents should determine if this type of interference is present in samples. Deuterium arc background correction is used to automatically correct for these interferences.

4.5 Daily monitoring test of the deionized water supply must have been performed and pass or meet appropriate criteria for analysis before the water can be used in sample preparation All glassware to be used in the analysis must be cleaned and rinsed thoroughly with DI water Periodic cleaning of sample preparation and analysis areas will be performed

5.0 RECORD KEEPING

5.1 Each analyst is responsible for keeping accurate and up-to-date records of all analyses performed.

5.2 Mercury Log Book:

A log book will be maintained for all mercury determinations. All information regarding samples processed in the lab will be entered into this book. This information will include but is not limited to

- Method reference number
- GLA Sample I D. (one complete for each set)
- Initial sample volume or weight used
- Final volume of digestates
- LIMS batch reference number
- Analyst's signature and date prepared/analyzed
- Sample matrix type
- Spiking volumes used
- Spike standard identifier
- Spike standard concentration
- LCS and matrix spike information
- Reviewer's signature and date
- Time/temperature of water bath (initial and every 30 minutes)
- Calibration standard identifiers and concentrations
- All readings, dilution factors, and calculated results

This log should also include any unique observations noted in regard to specific samples Space will be reserved on each page for calculations and notes All unused portions of logbook pages must be z'ed out.

5 3 Sample Schedule - All samples will be tracked through the lab using GLA sample I.D. numbers generated by the GLA LIMS system.

6.0 QUALITY CONTROL

6.1 QUALITY CONTROL SAMPLES

Quality control samples are run at a minimum 5 % frequency (*i e* one set with every batch of twenty or less samples). The results of these samples are used to gauge accuracy and precision of the method. These samples include method blanks (MB). lab control samples (LCS) matrix spikes (MS) and matrix spike duplicates (MSD) The quality control samples contain all reagents and are subjected to all preparation steps. They are processed and analyzed along with test samples.

6.2 METHOD BLANK

Matrix-matched method blanks (MB) containing all reagents and subjected to all preparation steps are processed and analyzed along with the samples. Method blanks must produce a concentration below the reporting limit (*e.g.* PQL, EQL. .) for an analytical batch to be valid These samples provide a measure of laboratory and/or reagent contamination. Test sample results are not corrected for the method blank concentrations.

6.3 LABORATORY CONTROL SAMPLE (LCS)

An external (independently sourced) reference standard is prepared within the working range of the method and analyzed with each matrix per batch of twenty or less samples (*i.e.* minimum 5 % frequency) The results of the samples must be within established control limits, or where there is not enough data to calculate control limits, within 15 % of the known value.

6.4 MATRIX SPIKED SAMPLES

Matrix spiked samples (MS and MSD) will be analyzed with a minimum frequency of 5 % (*e g.* one set per 20 or less samples per matrix) and are used to determine accuracy and precision of a method. The matrix spiked samples will be spiked using the same standards used to spike the LCS samples The analyzed result of the matrix spikes must be within established control limits, or where there is not enough data to calculate control limits, within 25 % of the known value

6.5 SURROGATE MATRIX BLANK AND SPIKED SAMPLES

In cases where no additional sample is available for matrix spiking (*e.g.* wipes samples), a set of surrogate matrix QC samples will be produced by digesting an appropriate substrate "blank" and two spiked samples of the same substrate spiked with the same standards and at the same levels of the LCS

6.6 QUALITY CONTROL TRACKING AND DATA REVIEW

The QC data is considered acceptable and actual samples results can be evaluated and reported by the analyst if all QC samples are within established control limits

6.7 CORRECTIVE ACTION

If a quality control measure fails, corrective action is taken and documented to ensure the accuracy of the data that is reported. Examples of when corrective action sheets are filled out are:

- A sample or QC is re-analyzed. This may be due to the QC parameter failing or mislabeling of samples.
- Samples are reported with a QC result (blank, spike matrix) parameter out of control. In this case, not only should a corrective action be initiated, but the data must be flagged
- A deviation from the normal SOP for the method is discovered (*e.g.* a digestion goes down to dryness or a different concentration of reagent is used) and the sample is analyzed and reported.
- An error in a previously reported sample is discovered

7.0 SAMPLE MANAGEMENT

7.1 The procedures for sample management are detailed in the Great Lakes Analytical SOP for sample receipt into the laboratory.

7.2 Sample Schedule. Analysts keep track of sample throughput by using the Laboratory Information Management System (LIMS). The system is checked daily and a hard copy generated Samples for mercury analysis are queued under "xxxx"=FLAA. The information includes:

- Client name
- Sample numbers
- Project name
- Matrix.
- Hold time and turnaround time.

8.0 METHOD VALIDATION

8.1 QUALITY CONTROL BOOK

Method validation must be performed before any actual samples can be analyzed Method validation studies are required to be stored in the QC logbook. Method exception studies must also be performed to validate any exception taken by proving equivalency with the unaltered method. The contents of the QC book include:

- Copy of the GLA Quality Assurance Program.
- Copies of GLA SOP and source methods.
- Copies of the calibration studies and dates in use.
- Copy of the precision and accuracy study for the method
- Copies of all method detection limit studies and dates in use
- Check standard recovery tabulations and control limits
- Spike and spike duplicate recovery tabulations and control limits
- Corrective action sheets.

8.2 QUALITY ASSURANCE PROGRAM

Internal audits will be performed periodically to assess analytical system performance Performance evaluation samples will be analyzed periodically to assess laboratory performance (Refer to the GLA Quality Assurance Program.)

8.3 METHOD DETECTION LIMIT STUDY

8.3.1 The method detection limit (MDL) is defined as the minimum concentration of analyte that can be determined with 99% confidence. It is determined as follows

- Prepare a minimum of seven replicate samples at a concentration at or near the expected MDL. Carry these replicates through the entire sample preparation procedure and analysis.

- Calculate the MDL by taking the standard deviation of the results of the 7 replicates and multiply by the Student's t value at n-1 degrees of freedom (3.143 for 7 replicates).

8.3.2 Other factors such as matrix effects and instrument noise may affect the attainable detection limit. These should be quantified if possible and taken in to account when determining an MDL as the obtainable detection level may be artificially elevated due to these factors

8 3 3 A new MDL study must be performed to re-evaluate the method if any major instrument maintenance or service is performed, if any new method exceptions or changes are made or at least annually

9.0 EQUIPMENT

9 1 Atomic absorption spectrophotometer - fitted with a mercury hollow cathode lamp, capable of allowing the absorption cell to be mounted in a stable fashion in the light path of the instrument, Varian 600 DBQ, and able to correct for non-atomic absorption at the selected analytical wavelength, or equivalent.
9 2 Absorption cell - 10 cm long with UV-transparent quartz windows.
9.3 Cold mercury vapor generator - for proper proportional mixing of mercury reducing agents and physical vapor generation. Varian VGA 77, or equivalent
9 4 300-mL capacity BOD bottle with stoppers.
9 5 Hot plate/water bath - capable of maintaining 95°C
9.6 Thermometer - to accurately monitor the water bath for range 95-100°C
9.7 Graduated cylinders. 100-mL size
9 8 Pipettors and tips. 5-10 mL size.
9 9 Analytical balance capable of weighing to nearest 0.1 g
9.10 5-20 mL dispensers with bottle.

10.0 STANDARDS AND REAGENTS

10 1 Reagent water - ASTM Type II or equivalent (DI water).
10.2 Sulfuric acid - concentrated H_2SO_4 Fisher no. A300 **CAUTION:** Sulfuric acid is corrosive
10.3 Nitric acid - concentrated HNO_3, Fisher no. A509. **CAUTION:** Nitric acid is corrosive
10.4 Hydrochloric acid - concentrated HCl, Fisher no A508 **CAUTION:** Hydrochloride acid is corrosive
10.5 Aqua regia. 50% - Prepare immediately before use First, make aqua regia by carefully adding 3 volumes of concentrated HCl to 1 volume of concentrated HNO_3 Then mix equal volumes of the aqua regia with reagent water. **CAUTION:** Aqua regia gives off extremely corrosive, irritating fumes All handling of aqua regia should be performed in a fume hood
10 5 Hydrochloric acid, 5 N - Dilute 40 mL of concentrated HCl to 100 mL with reagent water
10.6 Hydrochloric acid, 20% v/v - Dilute 20 mL of concentrated HCl to 100 mL with reagent water.
10.7 Potassium permanganate - $KMnO_4$ crystals, Fisher no. P279, or Mallinckrodt no. 7068. **CAUTION:** Oxidizer
10 8 Potassium permanganate solution - Dissolve 5 g of $KMnO_4$ per 100 mL of reagent water
10 9 Potassium persulfate - $K_2S_2O_5$, crystal, Merck no PX1560-1 or Mallinckrodt no 7076. **CAUTION:** Oxidizer.
10.10 Potassium persulfate solution - Dissolve 5 g of $K_2S_2O_5$ per 100 mL of reagent water
10 11 Hydroxylamine hydrochloride - $NH_2OH \cdot HCl$, crystals. Fisher no H330 or Mallinckrodt no
10 12 Sodium chloride - NaCl crystals, Fisher no. S271 or Mallinckrodt no 7581
10.13 Hydroxylamine hydrochloride solution - Dissolve 12 g of $NH_2OH \cdot HCl$ and 12 g of NaCl per 100 mL of reagent water
10 14 Stannous chloride, dihydrate - Tin (II) chloride dihydrate, $SnCl_2 \cdot 2 H_2O$ crystals, Fisher no T142, or Mallinckrodt no 3176.
10.15 Stannous chloride solution - Add 25 g of $SnCl_2 \cdot 2 H_2O$ per 100 mL of 20% v/v hydrochloric acid. Mix well to dissolve. Prepare fresh weekly. Discard if precipitation occurs

10.16 Mercury stock standard solutions, 1000 ppb - use 2 different suppliers for solutions "A" and "B": Ultra Scientific no. ICP-080, Fisher no. SM114, Mallinckrodt no. H548.

10.17 Mercury working standard solutions, 1 ppm (1000 ppb) - "A": Add 0.15 mL of concentrated HNO_3 to a 100-mL volumetric flask and add 50 mL of reagent water. Aliquot 0.10 mL of mercury stock standard solution "A" into the flask, dilute to the mark, and mix. Repeat for mercury spiking standard "B", except using mercury stock standard solution "B". Prepare fresh monthly.

11.0 PROCEDURE

NOTE: Method validation (section 8.0) must be performed before samples can be analyzed.

11.1 Assemble all materials and equipment required for the procedure. A daily calibration check of the analytical balance must have been performed prior to its use in weighing samples or standard materials. Record all pertinent sample information in the appropriate log book(s) ***before beginning analysis***.

11.2.1 Method Validation Study - A method validation study must be performed, including a method detection limit determination. (Refer to section 10.7 for details.)

11.2 PREPARATION OF QUALITY CONTROL AND TEST SAMPLES

11.2.1 For Method Blanks:

- Liquid samples - Aliquot 100 mL of reagent water into a BOD bottle.
- Solid samples - Place 0.5 g of clean sand into a BOD bottle.
- Wipe samples – Place a 15cm Whatman 41 filter paper into a BOD bottle.

11.2.2 For Laboratory Control Samples (samples contain 1.0 ppb Hg):

- Liquid samples - Aliquot 100 mL of reagent water into a BOD bottle. Accurately aliquot 0.10 mL of mercury spiking standard "B" into the bottle.
- Solid samples - Place 0.5 g of clean sand into a BOD bottle. Accurately aliquot 0.10 mL of mercury spiking standard "B" into the bottle.
- Wipe samples – Place a 15cm Whatman 41 filter paper into a BOD bottle. Accurately aliquot 0.10 mL of mercury spiking standard "B" into the bottle.

11.2.3 For Test Samples:

- Aqueous liquids - Aliquot a 100-mL portion of well-mixed sample in a BOD bottle.
- Non-aqueous liquids - Transfer a representative 10-50 mL aliquot of well-mixed sample into a BOD bottle. Add reagent water to the bottle to bring the total volume to 100 mL.
- Mixed liquids (aqueous/non-aqueous) - The sample should be well-mixed before pouring a representative aliquot. The analyst should use his/her own judgement in determining the proper aliquot size so as not to exceed 20% non-aqueous liquid in the sample. If less than 100 mL is used, add reagent water to bring the total volume to 100 mL.
- Solid samples - A representative 0.5 g portion of sample is weighed and placed in a BOD bottle (for samples with a high water content, be sure the sample is mixed thoroughly). For samples of mixed solid types, particle size reduction and mixing may be required to ensure that a representative sample is analyzed.
- Wipes samples - The entire wipe is placed into the BOD bottle, and the sample container rinsed into the BOD bottle with about 5ml of water.

11.2.4 For Matrix Spike Samples (samples have 1.0 ppb Hg added):

- Liquid samples - Aliquot two additional 100-mL portions of one sample, making sure to sample as homogeneous a mixture as possible. Accurately aliquot 0.10 mL of mercury spiking standard "B" into each replicate. Mark as MS and MSD.
- Non-aqueous liquids - Transfer two additional representative 10-50 mL aliquots of well-mixed sample into BOD bottles. Add reagent water to the bottles to bring the total

volume to 100 mL. Accurately aliquot 0.10 mL of mercury spiking standard "B" into each bottle, and label as MS and MSD.

- Mixed liquids (aqueous/non-aqueous) - The sample should be well-mixed before pouring a representative aliquot. Do not exceed 20% non-aqueous liquid in the sample. If less than 100 mL is used, add reagent water to bring the total volume to 100 mL. Accurately aliquot 0.10 mL of mercury spiking standard "B" into each bottle, and mark as MS and MSD.
- Solid samples - Two additional representative 0.5 g portions of one sample are weighed and placed into BOD bottles. Accurately aliquot 0.10 mL of mercury spiking standard "B" into each bottle and label as MS and MSD.
- Wipes samples - Two additional wipes are placed into two BOD bottles (1 each), and the sample containers rinsed with a minimum amount of reagent water. Accurately aliquot 0.10 mL of spiking standard "B" into each bottle. Mark as MS and MSD.

11.3 PREPARATION OF CALIBRATION AND CHECK STANDARDS

11.3.1 Add 100 mL of reagent water to each of 6 BOD bottles. Aliquot 0.00, 0.05, 0.10, 0.15, 0.20, and 0.25 mL of mercury working standard "A" into the bottles to produce a set of calibration standards of 0.00, 0.50, 1.00, 1.50, 2.00, and 2.50 ppb mercury.

11.3.2 Add 100 mL of reagent water and 0.10 mL of mercury spiking standard "B" to a BOD bottle, producing a 1.0 ppb check standard.

11.4 DIGESTION OF LIQUIDS

See section 11.5 for digestion of solids.

CAUTION: The heated reaction in the BOD bottles produces gases and steam which will cause significant pressure. Bottle stoppers should be wet with water prior to placing in the bottle necks to prevent freezing up and allowing the samples to outgas.

11.4.1 Carry all standards and samples through all steps of the digestion procedure.

11.4.2 Add 5 mL of concentrated H_2SO_4 and 2.5 mL of concentrated HNO_3, mixing after each addition.

11.4.3 Add 15 mL of potassium permanganate solution. Allow samples to stand for 15 minutes. If the purple color fades, add additional permanganate noting in the log book how much additional permanganate has been added. Once the purple color has persisted for 15 minutes proceed to the next step.

11.4.4 Add 8 mL of potassium persulfate solution, and place in the water bath for 2 hours at 95-100°C. Monitor and record the temperature of the water bath initially and every 30 minutes, adding boiling water to the bath as necessary to keep the bath level above the level of sample in the BOD bottles.

11.4.5 After the heating period, remove the sample bottles, cool, and add 6 mL of hydroxylamine hydrochloride solution (reduces excess permanganate).

11.5 DIGESTION OF SOLIDS

See section 11.4 for digestion of liquids.

CAUTION: The heated reaction in the BOD bottles produces gases and steam which will cause significant pressure. Bottle stoppers should be wet with water prior to placing in the bottle necks to prevent freezing up and allowing the samples to outgas.

11.5.1 Carry all standards and samples through all steps of the digestion procedure.

11.5.2 For solids. Add 10 mL of 50% *aqua regia*. Heat in a water bath at 95°C for 2 minutes.

11.5.3 Cool, and add 50 mL of reagent water and 15 mL of potassium permanganate solution.

11.5.4 Place in the water bath for 30 minutes at 95-100°C.

11.5.5 After the heating period, remove the sample bottles, cool, and add 6 mL of hydroxylamine hydrochloride solution (reduces excess permanganate). Add 50 mL of reagent water and mix.

11.6 ANALYTICAL PROCEDURE

11.6.1 Refer to the manufacturer's instruction manual for instrument set-up and operation. See Appendix B for a condensed list of operating instructions.

11.6.2 Calibration - The analyst will be prompted for the calibration blank and each standard in turn. The digests will be processed and analyzed by the instrument and the resultant absorbencies used to construct a calibration curve. The curve must have a correlation coefficient of 0.995 or greater to be valid. If not, the instrument will attempt a second calibration. If this fails, the operator must stop the run and determine the problem and correct before continuing.

11.6.3 A typical batch is analyzed according to the following protocol:

1) Calibration blank - result must be < detection level (0.0002 ppb).
2) Initial check standard - result must be within ± 10%
3) Repeat check standard (optional) - same as check standard;
4) High calibration standard - result must be within ± 10%, or within established control limits;
5) Method blank - result must be < detection level (0.0002 ppb).
6) LCS samples - result must be within ± 15%, or within established control limits;
7) Unspiked matrix test sample;
8-9) Matrix spikes - result must be within ± 25% or within established control limits;
10+) Balance of test samples. Include a check standard every 10 samples (or less) - the check standard must be ± 20%, or the run paused, problem corrected, and any samples run since the last passing check standard re-analyzed.

NOTE: Samples with a high level of suspended solids may require settling or filtration prior to analysis to prevent blockage of the pump tubing.

11.6.4 If a sample analysis is significantly high out of range, and "poisoning" of the system is suspected a reagent blank should be analyzed repeatedly until it produces results below the reporting limit. If this isn't accomplished, the system is cleaned, recalibrated, and the affected samples reanalyzed.

11.7 CALCULATIONS

After a run has been completed and all of the verification standards are in control, the data may be calculated and reported.

For liquids:

$$mg/L\ Hg = \frac{analyzed\ concentration \cdot dilution\ factor \cdot 100 \cdot volume\ used\ (mL)}{1000}$$

$$detection\ limit\ (DL,\ mg/L) = \frac{0.2 \cdot 100\ /\ volume\ used\ (mL)}{1000}$$

For solids:

$$mg/kg\ Hg = \frac{analyzed\ concentration \times dilution\ factor \times 100\ /\ weight\ used\ (g)}{1000}$$

$$detection\ limit\ (DL,\ mg/L) = \frac{0.2 \times 100\ /\ weight\ used\ (g)}{1000}$$

The dilution factor is 1, unless additional dilution of the sample was done.
"1000" is the conversion factor for ppb to ppm (mg/L)

12.0 MAINTENANCE AND TROUBLESHOOTING

12.1 GENERAL

Glassware should be cleaned appropriately to avoid sample contamination. See Appendix C for glassware cleaning instructions. Equipment should be kept clean and maintained to avoid sample contamination and assure proper operation. Manuals supplied by the manufacturers with the instrumentation typically have informational and troubleshooting sections.

12.2 TECHNICAL SUPPORT

Technical support is available from equipment manufacturers (for example, by telephone, fax, or e-mail). They can be a good resource when troubleshooting options have been exhausted. Technical support departments can readily supply part numbers.

13.0 REFERENCES

13.1 EPA Methods 245.1, Mercury (Manual Cold Vapor Technique), and 245.5, Mercury in Sediment (Manual Cold Vapor Technique).

13.2 Method 3112, Metals by Cold-Vapor Atomic Absorption Spectrometry, Section B (Mercury); Standard Methods for the Examination of Water and Wastewater, 18th Edition, 1992.

13.3 Methods SW-846 - 7470A: Mercury in Liquid Waste (Manual cold-vapor technique); and 7471A: Mercury in Solid or Semisolid Waste (Manual cold-vapor technique).

13.3 Great Lakes Analytical Quality Assurance Program Manual.

13.4 Great Lakes Analytical Chemical Hygiene Plan.

13.5 Great Lakes Analytical SOP for Login Department.

13.6 Great Lakes Analytical SOP for Hazardous Sample Management.

14.0 DEFINITIONS

See References.

APPENDIX A.

METHOD EXCEPTIONS.

A.1 A semi-automated continuous-flow mercury vapor (hydride generator) is used to produce the cold mercury vapor. The automatic nature of the peristaltic pump and mixing manifold provides much enhanced stability and consistency in absorbance readings.

A.2 A calibration range more appropriate to the detection levels required and concentrations of routine samples has been selected at 0.0 to 2.5 ppb.

A.3 For solids, a single 0.5 g portion of sample is used for the analysis. Past performance of P.E. samples and replicate data has shown this procedure to produce accurate and precise results.

A.4 The dead air space in the BOD bottle does not need to be purged before processing the sample through the cold-vapor generator because the final reaction does not occur in the BOD bottle.

APPENDIX B.

CONDENSED FLAA OPERATING INSTRUCTIONS

B.1 Sequence
- Modify an existing sequence
- OK

B.2 Select sequence
- Mercury 05/27/97. Hex Chrome
- OK
- 4 Hg Vapor, 99 Cr Flame Hexachrome
- Error protocc
- Next
- Exit and switch to instrument window
- OK

B.3 Optimize
- Rescale
- Instrument zero

B.4 Return:
- Start autorun
- Metal - Matrix - Date
- Analyst's intitials
- OK
- Prompt Present Rinse
- OK
- Calibrate 0 0, 0.5, 1.0, 1.5, 2.0, 2.5 ppb

APPENDIX C.

METALS GLASSWARE PREPARATION

All glassware to be used in the preparation of solutions for metals analysis will be prepared according to the following procedure

1. All beakers, funnels, flasks, stoppers and watch covers will be examined for gross contamination and soil removal.

2. Any analyst processing glassware through the laboratory dishwasher will use the appropriate detergent supplied.

3. All glassware shall subsequently be *hand-washed* using Neutrad soap (anionic detergent) and triple rinsed with tap water, then triple rinsed with de-ionized water, paying special attention to any glassware unduely etched, cracked or otherwise likely break and/or cause contamination of samples.

4. All glassware which will come into contact with samples to be analyzed for metals will be rinsed with a 50% Nitric Acid solution and triple rinsed with de-ionized water immediately prior to use. Glassware to be used for other inorganic analyses should be rinsed with an acid appropriate to the test. (e.g. - dilute sulfuric for nitrate/nitrite) and triple rinsed with de-ionized water.

Standard Operating Procedure for the Determination of Total Cyanide and Cyanide Amenable to Chlorination in Liquids and Solids

GREAT LAKES ANALYTICAL

STANDARD OPERATING PROCEDURE

FOR

THE DETERMINATION OF TOTAL CYANIDE

AND CYANIDE AMENABLE TO CHLORINATION

IN LIQUIDS AND SOLIDS

GLA 335.4 BG

Revision 2.0

Approved By:

Department Manager: _____ Date: 10/27/98

Quality Assurance Manager: _____ Date: 10/27/98

Laboratory Director: _____ Date: 10-27-98

1.0 APPLICABILITY

This standard procedure (SOP) provides instructions for the handling, digestion, and distillation of liquid and solid samples for the analysis of total cyanide and cyanide amenable to chlorination. This SOP is an interpretation of EPA Method 335.4, Standard Methods no. 4500-CN⁻, and SW-846 Methods 9010B and 9012A.

1.1 MATRICES

This SOP may be used for drinking, ground, surface and saline waters, domestic and industrial waste, (solid, and mixed samples). Concentration range for samples is typically 5 to 1000 µg/L Higher concentrations may be determined by sample dilution. Samples are preserved by addition of 2 mL of 10 N sodium hydroxide per liter and refrigeration.

NOTE: Distillates and solutions produced for this SOP are only applicable for the analysis method specified and are unacceptable for any other anionic or cationic analyses

1.2 REGULATORY APPICABILITY

40 CFR 121

2.0 SUMMARY

Samples are tested and pre-treated for interferences, and then refluxed with sulfuric acid Cyanide is released from the sample as volatile hydrocyanic acid (hydrogen cyanide, or HCN) and absorbed in a gas scrubber containing sodium hydroxide. Cyanide in the distillates is converted to cyanogen chloride (CNCl) by reaction with chloramine-T. CNCl forms a red-blue dye color upon the addition of a pyridine-barbituric acid reagent. The absorbance of this dye is measured at 580 nm.

For the analysis of total cyanide, the sample is treated for interferents and distilled directly. For the determination of cyanides amenable to chlorination, duplicate samples are portioned out. One sample is treated with excess chlorine (as calcium hypochlorite) for one hour. The excess hypochlorite is destroyed with sodium arsenite and total cyanide determined for both treated and untreated samples. The amenable cyanide is the total cyanide less the residual cyanide determined on the chlorinated sample.

3.0 SAFETY

3.1 GENERAL

This SOP does not address all safety issues associated with its use. A reference file of material safety data sheets (MSDS's) is available to all personnel, along with the Great Lakes Analytical Chemical Hygiene Plan

The toxicity or carcinogenicity of each reagent used in this SOP has not been precisely determined; however, each chemical should be treated as a potential health hazard Exposure to these chemicals should be reduced to the lowest possible level Gloves are worn when handling solvents

3.2 CHEMICAL HYGIENE PLAN

The Great Lakes Analytical Chemical Hygiene Plan (CHP) is designed to establish safe work procedures and minimize exposure to hazardous chemicals encountered in the laboratory. The CHP

provides information to employees regarding potential hazards and training to minimize these hazards.

3.3 HAZARDOUS SAMPLES

All samples that are received by the laboratory have the possibility of containing hazardous pollutants. They should be treated with caution at all times. Gloves are worn when handling samples. Also see the Great Lakes Analytical SOP for Hazardous Sample Management.

3.4 METHOD SPECIFIC CHEMICALS

Cyanide is acutely toxic, and in the presence of acid produces highly toxic and volatile HCN (hydrocyanic acid) fumes. All handling of cyanide solutions and salts will be performed with proper gloves and ventilation. All fumes produced by the distillation procedure will be evacuated to an appropriate hood or ventilation source. When performing the amenable cyanide preparation, cyanides react with chlorine to produce CNCl (cyanogen chloride) which is extremely toxic. All amenable cyanide preparations will be performed in a fume hood.

Pyridine is a toxic organic which has a permeating, irritating odor. It is readily absorbed through the respiratory tract and skin. Operations involving large amounts of pyridine will be carried out in a fume hood and proper gloves should be worn. Waste from the analytical process containing pyridine should be covered with parafilm to minimize volatilization of the material.

4.0 INTERFERENCES

4.1 Several different interferences are encountered with this method. Most are removed by the distillation process. Those interferences requiring pre-treatment or special treatment of the sample are addressed below.

4.2 Sulfides produce hydrogen sulfide during the distillation which adversely affects colorimetric titrimetric, and electrode procedures. Samples are tested for sulfides with lead acetate paper. Bismuth nitrate solution is added to samples testing positive for sulfides to remove the interference.

4.3 Oxidizing agents such as chlorine decompose most cyanides. Samples are tested for oxidizers with KI-starch paper. Samples exhibiting positive results for oxidizers are treated with ascorbic acid until a negative test for oxidizers is obtained.

4.4 Nitrate and nitrite may produce a high bias to results. These ions produce nitrous acid which in turn can react with certain organic compounds to produce oximes. These oximes decompose to generate HCN. Interference from nitrates and nitrites is removed by the addition of sulfamic acid to the sample.

4.5 Carbonate in high concentrations may affect the distillation procedure by causing the violent release of carbon dioxide with excessive foaming when acid is added before distillation. Calcium hydroxide may be used to preserve such samples.

5.0 RECORD KEEPING

5.1 The analyst is responsible for keeping accurate and up-to-date records of all distillations and analyses performed.

5.2 Total Cyanide Log Book

A log book will be maintained for all cyanide distillations and determinations. All information regarding samples processed in the lab will be entered into this book. This information will include but is not limited to:

- Method reference number
- Client Name for each set of samples
- GLA Sample I.D. (one complete for each set)
- Initial sample volume or weight used
- LIMS batch reference number
- Analyst's signature and date prepared/analyzed
- Data reviewer's signature and date
- Calibration standard identifiers and concentrations
- All readings, dilution factors, and calculated results
- Sample matrix type
- Spiking volumes used
- Spike standard identifier
- Spike standard concentration
- LCS and matrix spike information
- Final distillate volume

This log should also include any unique observations noted in regard to specific samples. Space will be reserved on each page for calculations and notes. All unused portions of logbook pages must be z'ed out. Examples of a log book cover page and reagent preparation sheets are provided in Appendix A of this SOP.

5.3 Sample Schedule - All samples will be tracked through the lab using GLA sample I.D numbers generated by the GLA LIMS system.

6.0 QUALITY CONTROL

6.1 QUALITY CONTROL SAMPLES

Quality control samples are run at a minimum 5% frequency (*i.e.* one set with every batch of twenty or less samples). The results of these samples are used to gauge accuracy and precision of the method. These samples include method blanks (MB), lab control samples (LCS), matrix spikes (MS) and matrix spike duplicates (MSD). The quality control samples contain all reagents and are subjected to all preparation steps. They are processed and analyzed along with test samples.

6.2 METHOD BLANK

Matrix-matched method blanks (MB) containing all reagents and subjected to all preparation steps are processed and analyzed along with the samples. Method blanks must produce a concentration below the reporting limit (*e.g.* PQL, EQL, ...) for an analytical batch to be valid. These samples provide a measure of laboratory and/or reagent contamination. Test sample results are not corrected for the method blank concentrations.

6.3 LABORATORY CONTROL SAMPLE (LCS)

An external (independently sourced) reference standard is prepared within the working range of the method and analyzed with each matrix per batch of twenty or less samples (*i.e.* minimum 5 % frequency). The results of the samples must be within established control limits, or where there is not enough data to calculate control limits, within 15% (10% for drinking waters) of the known value.

6.4 MATRIX SPIKED SAMPLES

Matrix spiked samples (MS and MSD) will be analyzed with a minimum frequency of 5% (*e.g.* one set per 20 or less samples per matrix) and are used to determine accuracy and precision of a method. The matrix spiked samples will be spiked using the same standards used to spike the LCS samples.

The analyzed result of the matrix spikes must be within established control limits, or where there is not enough data to calculate control limits, within 25% of the known value

6.5 SURROGATE MATRIX BLANK AND SPIKED SAMPLES

In cases where no additional sample is available for matrix spiking (*e.g.* wipes samples), a set of surrogate matrix QC samples will be produced by digesting an appropriate substrate "blank" and two spiked samples of the same substrate spiked with the same standards and at the same levels of the LCS.

6.6 QUALITY CONTROL TRACKING AND DATA REVIEW

The QC data is considered acceptable and actual samples results can be evaluated and reported by the analyst if all QC samples are within established control limits

6.7 CORRECTIVE ACTION

If a quality control measure fails, corrective action is taken to document steps taken to ensure the accuracy of the data that is reported. Examples of when corrective action sheets are filled out are:

- A sample or QC is re-analyzed. This may be due to the QC parameter failing or mislabeling of samples.
- Samples are reported with a QC result (blank, spike matrix) parameter out of control. In this case, not only should a corrective action be initiated, but the data must be flagged.
- A deviation from the normal SOP for the method is discovered (*e.g.* a digestion goes down to dryness or a different concentration of reagent is used) and the sample is analyzed and reported.
- An error in a previously reported sample is discovered.

7.0 SAMPLE MANAGEMENT

7.1 The procedure for sample management are detailed in the Great Lakes Analytical SOP for sample receipt into the laboratory.

7.2 Sample Schedule. Analysts keep track of sample throughput by using the Laboratory Information Management System (LIMS). The system is checked daily and a hard copy generated. Samples for this method are queued under "AUTO". The information includes

- Client name.
- Sample numbers.
- Project name
- Matrix
- Hold time and turnaround time.

8.0 METHOD VALIDATION

8.1 QUALITY CONTROL BOOK

Method validation must be performed before any actual samples can be analyzed. Method validation studies are required to be stored in the QC logbook. Method exception studies must also be performed to validate any exception taken by proving equivalency with the unaltered method. The contents of the QC book include:

- Copy of the GLA Quality Control Manual.
- Copies of GLA SOP and source methods.
- Copy of the precision and accuracy study for the method.
- Copies of all method detection limit studies and dates in use.
- Check standard recovery tabulations and control limits.

- Spike and spike duplicate recovery tabulations and control limits.
- Corrective action sheets.

8.2 INTERNAL AUDITS AND PERFORMANCE EVALUATION SAMPLES

Internal audits will be performed periodically to assess analytical system performance Performance evaluation samples will be analyzed periodically to assess laboratory performance. (Refer to the GLA Quality Assurance Plan.)

8.3 METHOD DETECTION LIMIT STUDY

8 3 1 The method detection limit (MDL) is defined as the minimum concentration of analyte that can be determined with 99% confidence. It is determined as follows:

- Prepare a minimum of seven replicate samples at a concentration at or near the expected MDL. Carry these replicates through the entire sample preparation procedure and analysis.
- Calculate the MDL by taking the standard deviation of the results of the seven replicates and multiply by the Student's t value at n-1 degrees of freedom (3.143 for seven replicates)

8.3.2 Other factors such as matrix effects and instrument noise may affect the attainable detection limit. These should be quantified if possible and taken in to account when determining an MDL as the obtainable detection level may be artificially elevated due to these factors.

8 3 3 A new MDL study must be performed to re-evaluate the method if any major instrument maintenance or service is performed if any new method exceptions or changes are made or at least annually.

9.0 EQUIPMENT

9 1 Glassware required for each distillation set-up:

- 500-mL round bottom boiling flask.
- Two-neck Claisen adapter with 24/40 ground glass joints.
- Allhin condenser with 24/40 ground glass joints.
- Tubing adapter with PTFE stopcock.
- 125-250 mL gas scrubbing bottle.
- Gas scrubber/stopper with fritted end.
- 300-mm thimble top tube funnels
- 100-250 mL volumetric flasks.
- 100-250 mL graduated cylinders.

9 2 Heating mantle(s) for 500-mL round bottom flasks with adjustable temperature control

9.3 Tygon tubing for connecting glass apparatus.

9.4 Analytical balance capable of weighing to the nearest 0.1 grams.

9 5 Lachat Quikchem AE Auto analyzer - capable of delivering and reacting samples and reagents for automated continuous flow analysis, including:

- Sampling device
- Multi-channel pump
- Reaction/mixing manifold for cyanide
- Colorimetric detector.
- Data acquisition device (computer)

9.6 Lead acetate paper, Fisher no. 14-862.

9.7 Potassium iodide (KI)-starch paper, Fisher no. 14-860

9.8 Teflon-coated stir bars and magnetic stir plate.

10.0 STANDARDS AND REAGENTS

10.1 Reagent water - ASTM Type II or equivalent (DI water).

10.2 Ascorbic acid - crystal, ACS, analytical reagent grade, or USP, Mallinckrodt no. 1852.

10.3 Bismuth nitrate pentahydrate - $Bi(NO_3)_3 \bullet 5\ H_2O$, Fisher no. B337, or Mallinckrodt no. 0256.

10.4 Bismuth nitrate, 0.062 M - Dissolve 30.0 g of $Bi(NO_3)_3 \bullet 5\ H_2O$ into 100 mL of reagent water in a 1-L reagent bottle. Add 250 mL of glacial acetic acid while stirring. Dilute to 1 L with reagent water and mix.

10.5 Calcium hypochlorite - $Ca(OCl)_2$, Fisher no. C100

10.6 Calcium hypochlorite, ~5% - Dissolve 50 g of $Ca(OCl)_2$ in 1000 mL of reagent water. Store protected from light exposure for up to one month.

10.7 Sodium hydroxide - NaOH pellets, Fisher no. S318, or Mallinckrodt no. 7708. **CAUTION:** Sodium hydroxide is corrosive.

10.8 Sodium hydroxide solution, 1.25 N - Dissolve 50 g of NaOH per liter of reagent water.

10.9 Sulfamic acid - H_2NSO_3H, Fisher no. A295, or Mallinckrodt no. 1931.

10.10 Sulfamic acid solution, 0.4 N H_2NSO_3H - Dissolve 40 g of H_2NSO_3H in 1 L of reagent water.

10.11 Sulfuric acid - concentrated H_2SO_4, Fisher no. A300. **CAUTION:** Sulfuric acid is corrosive.

10.12 Sulfuric acid, 18 N - Carefully dilute 500 mL of concentrated H_2SO_4 into 500 mL of reagent water, or use purchased 50% v/v (Fisher LabChem no. LC25640).

10.13 Magnesium chloride hexahydrate - $MgCl_2 \bullet 6\ H_2O$, Fisher no. M33, or Mallinckrodt no. 5958.

10.14 Magnesium chloride solution - Dissolve 510 g of $MgCl_2 \bullet 6\ H_2O$ per liter of reagent water.

10.15 Sodium arsenite - $NaAsO_2$, Fisher no. S225I. **CAUTION:** Arsenic compounds are toxic!

10.16 Sodium arsenite solution, 2% (w/v) $NaAsO_2$ - Dissolve 2 g of $NaAsO_2$, into 100 mL of reagent water.

10.17 Stock cyanide solutions - Calibration and spiking/check standards are prepared separately from independent sources of potassium cyanide (KCN, for example Fisher no. P223I, Mallinckrodt no. 6881). **CAUTION: Poison!** Standards expire one year from date of preparation.

- Weigh ~260 mg of potassium cyanide (KCN) and 0.1-0.2 g NaOH (several pellets) into a 1-L volumetric flask, dissolve in reagent water, dilute to the mark and mix. This solution is approximately 100 ppm CN^-. Label this solution calibration standard "A". Actual concentration is determined titrimetrically per Appendix B.
- Weigh ~260 mg of potassium cyanide (KCN) and 0.1-0.2 g NaOH (several pellets) into a 1-L volumetric flask, dissolve in reagent water, dilute to the mark and mix. This solution is approximately 100 ppm CN^-. Label this solution calibration standard "B". Actual concentration is determined titrimetrically per Appendix B.

10.18 Standard silver nitrate solution(s), 0.01-0.02 N $AgNO_3$ - for example, Fisher (LabChem) no. 22630, Mallinckrodt no. H394. Solutions from two sources required.

10.19 p-Dimethylaminobenzalrhodanine - Aldrich no. 11,458-8, or Mallinckrodt no. 2754.

10.20 Acetone - reagent grade, Fisher no. A18.

10.21 Indicator solution - Dissolve 20 mg of p-dimethylaminobenzalrhodanine in 100 mL of acetone.

10.22 Barbituric acid - Aldrich no. 18,569-8, or Mallinckrodt no. 2046.

10.23 Pyridine - C_5H_5N, Fisher no. P368. **CAUTION:** Strong odor.

10.24 Hydrochloric acid - concentrated HCl, Fisher no. A508. **CAUTION:** Hydrochloric acid is corrosive.

10.25 Pyridine-barbituric acid reagent - Weigh 15 g of barbituric acid into a 1-L reagent bottle. Rinse down the sides and wet with about 100 mL of reagent water. In a fume hood, add 75 mL of pyridine, and mix thoroughly. Carefully add 15 mL of concentrated HCl and mix. Transfer to a 1000-mL volumetric flask and dilute to the mark with reagent water. Mix until all of the barbituric acid has dissolved. This solution should have a pale straw color. A dark orange or yellow indicates improper preparation and reagent needs to be re-prepared. This solution is stable for six months.

10.26 Sodium phosphate, monobasic, monohydrate - $NaH_2PO_4 \bullet H_2O$, Fisher no. S369.

10.27 Sodium dihydrogen phosphate buffer, 1 M - Dissolve 138 g of $NaH_2PO_4 \bullet H_2O$ in 1 L of reagent water. Store refrigerated.
10.28 Chloramine-T, Mallinckrodt no. 0614-58.
10.29 Chloramine-T solution - Dissolve 2.0 g of chloramine-T in 500 mL of reagent water.
10.30 Glacial acetic acid, CH_3COOH, Fisher no. A38.
10.31 Dilute acetic acid - Dilute 1 mL of glacial acetic acid to 100 mL with reagent water.

11.0 PROCEDURE

NOTE: Method validation (section 8.0) must be performed before samples can be analyzed.

11.1 Assemble all materials and equipment required for the procedure. A daily calibration check of the analytical balance must have been performed prior to its use in weighing samples or standard materials. Record all pertinent sample information in the log book(s) ***before beginning the analysis***.

11.2 PREPARATION OF QUALITY CONTROL AND TEST SAMPLES

11.2.1 For Method Blanks:
- Liquid samples - Aliquot 250 mL of reagent water into a clean 500-mL round bottom flask.
- Solid samples - Weigh 10 g of clean sand into a clean 500-mL round bottom flask. Add 250 mL of reagent water.

11.2.2 For Laboratory Control Samples (samples contain approximately 400 ppb CN^-).
- Liquid samples - Aliquot 250 mL of reagent water into a clean 500-mL round bottom flask. Accurately aliquot 1.0 mL of spiking standard 'B' into the flask.
- Solid samples - Weigh 10 g of clean sand into a clean 500-mL round bottom flask. Add 250 mL of reagent water. Accurately aliquot 1.0 mL of spiking standard 'B' into the flask.

11.2.3 For Test Samples:
- Aqueous liquids - A representative 250 mL aliquot of sample is placed into a clean 500-mL round bottom flask. (If high cyanide content is expected, a proportionally smaller sample can be used. Bring the total volume to 250 mL with reagent water.)
- Non-aqueous liquids - Transfer a representative 25 g portion of well mixed sample into a clean 500-mL round bottom flask. Add 225 mL of reagent water to the flask.
- Mixed liquids (aqueous/non-aqueous) - The sample should be well mixed before pouring a representative aliquot. The analyst should use his/her own judgment in determining the proper aliquot size so as not to exceed 20% (50 mL) of non-aqueous portion of sample. If less than 250 mL is used, reagent water is added to bring the total volume to 250 mL.
- Solid samples - A representative 10 g portion of sample is weighed into a clean 500-mL round bottom flask. Mixed solids may require particle size reduction to assure a homogeneous sampling of all solids in the sample. Add 250 mL of reagent water to the flask.

11.2.4 For Matrix Spike Samples (samples have approximately 400 ppb CN^- added):
- Liquid samples - Measure two additional 250 mL aliquots of one sample, making sure to sample as homogeneous a mixture as possible. Accurately aliquot 1.0 mL of spiking standard "B" into the replicate samples, and mark them as MS and MSD.
- Solid samples - Weight two additional aliquots of one sample making sure to sample as homogeneous a mixture. Add 250 mL of reagent water to each flask. Accurately aliquot 1.0 mL of spiking standard "B" - into the replicate samples, and mark them as MS and MSD.

11.2.5 Add several boiling chips to every sample.

NOTE: All samples must be screened for sulfide and oxidants!

11.3 SAMPLE SCREENING AND PRE-TREATMENTS

11.3.1 Sulfide:

- Screening is performed by placing several drops of a water sample or of the soil/water slurry on a strip of lead acetate paper which has been moistened with dilute acetic acid. A blackening of the paper indicates the presence of sulfides, and the sample must be treated prior to distillation.
- Pre-treat for sulfides by adding 25 mL of bismuth nitrate solution to the sample and mixing for 5 minutes before starting distillation

11.3.2 Oxidants:

- Screening is performed by placing several drops of a water sample or of the soil/water slurry on a strip of KI starch paper. A darkening or blue color of the paper indicates the presence of chlorine or other oxidants, and the sample must be treated prior to distillation.
- Pre-treat for oxidants by adding small amounts of ascorbic acid to the sample until a negative result is obtained for the KI-starch paper test. Then add an additional ~0.5 g of ascorbic acid.

11.3.3 Samples screened for sulfides and oxidants are now ready for distillation and/or pre-treatment for cyanide amenable to chlorination (sections 11.4 and 11.5)

11.4 CHLORINATION OF SAMPLES

This treatment only for samples of cyanides amenable to chlorination.

NOTE: This procedure must be performed under amber or reduced lighting. Potassium ferricyanide may decompose under fluorescent lighting or sunlight, producing a positive result for cyanide amenable to chlorination.

11.4.1 Prepare two identical replicate samples for total cyanide. Reserve one replicate for a normal total cyanide analysis.

11.4.2 To the other replicate, in a hood, add small amounts of a 5% calcium hypochlorite solution to the sample while stirring on a magnetic stir plate until an excess of hypochlorite is present, as indicated by a positive KI-starch paper test

11.4.3 Test the sample every ten minutes and maintain an excess of hypochlorite on the sample for one hour

11.4.4 Add 1 mL portions of 0.1 N sodium arsenite solution until KI-starch paper indicates no residual chlorine. Add an additional 5 mL of 0.1 N sodium arsenite solution to ensure an excess of reducing agent

11.4.5 Samples screened for oxidants, sulfides, and treated for amenable cyanides are now ready for distillation (section 11.5).

11.5 DISTILLATION PROCEDURE

11.5.1 Assemble each digestion unit in accordance with Figure 1.

11.5.2 Aliquot 50 mL of 1.25 N NaOH into each scrubber bottle, and add enough reagent water to cover the fritted glass bubbler on the end of the stem. Close the stopcock valve on the adapter.

11.5.3 When all scrubbers have been prepared, switch on the vacuum pump and adjust the stopcock valve on each set-up to allow a slow stream of air to pass through the system. Adjust the valve so that roughly two bubbles per second enter the 500 mL digestion flask through the end of the tube funnel.

11.5.4 Add distillation reagents:

- 25 mL of sulfamic acid solution to each sample through the tube funnel. Allow to mix for three minutes minimum.
- 25 mL of 18 N H_2SO_4 to each sample.
- 10 mL of 2.5 M $MgCl_2$ solution to each sample.

11.5.5 Distill samples:

- Switch on heating mantles and set to high.
- Note the time that each sample begins boiling to the nearest 5 minute interval, and note on the flask with a marking pen.
- Continue refluxing for one hour. Turn off mantle(s) and continue the airflow for at least 15 minutes.
- Allow the boiling flask to cool, dislodge the tube funnel stopper and close the vacuum valve.
- Quantitatively transfer the scrubber solutions into clean 250-mL volumetric flasks and dilute to the mark with reagent water. The distillates are now ready for automated (LACHAT) or manual colorimetric (Milton-Roy SPEC 20) analysis.

NOTE: If samples are not to be run on the same day distilled, the distillates are stored in the refrigerator, or transferred to plastic sample cups and stored refrigerated.

11.6 PREPARATION OF CALIBRATION AND CHECK STANDARDS

11.6.1 Calibration standards are prepared by serial dilutions of stock standard "A". Note that final concentrations of the standards depend upon the concentration of the calibration source standard as determined titrimetrically (Appendix B). (Sodium hydroxide is added to each standard to matrix match the standards with the distillates.) Prepare standard set per Table 1.

Table 1.
Preparation of Calibration Standards.

Standard Level	Volume Stock Standard (mL)	Final Volume (mL)	Volume 1.25 N NaOH (mL)	Approx. CN^- Concentration (ppb)
A	1.0	100	20	1000
B	0.5	100	20	500
C	0.2	100	20	200
D	0.1	100	20	100
E	0.05	100	20	50
F	0.025	100	20	25
G	0.010	100	20	10
H	0.00	100	20	0

11.6.2 Check Standard - A Check Standard is prepared fresh daily. The check standard is prepared by aliquoting 0.5 mL of Spiking Source Standard "B" into a 100-mL volumetric flask, adding 20 mL of 1.25 N NaOH, diluting to the mark with water, and mixing. This check standard contains approximately 500 ppb cyanide. Reserve the previous check standard as it will also be evaluated with the run as the "old check standard".

NOTE: At client request, high and low standards may be distilled along with samples. The concentrations of the distilled check standards should be ± 10% of the undistilled standards.

11.7 OPERATION OF THE LACHAT ANALYZER

11.7.1 Power up the Lachat analyzer in accordance with the manufacturer's instructions. **Allow the system to warm up at least 15 minutes.**

11.7.2 Install the cyanide manifold, sample loop, and filter, making sure that all connections have been made and properly tightened.

11.7.3 Place the reagent uptake tubes in their appropriate reagent bottles and prime the system while checking for leaks.

11.7.4 Pour an aliquot of each Calibration Standard (A-H) into 6-mL disposable culture tubes and place in the corresponding sampler positions (see Table 2).

Table 2.
Positions of Samples in the Analyzer.

Position	Sample	Position	Sample	Position	Sample
1	Blank	5	High Cal Std	9	Matrix Spike
2	Blank	6	Blank	10	Matrix Spike Duplicate
3	Old Check Std	7	Method Blank	11	Matrix Sample
4	New Check Std	8	LCS	12	Blank

11.7.5 The remaining samples from the batch are loaded into the sampler with a Check Standard and Calibration Blank every ten or less samples, including the QC spikes and samples.

11.7.6 Select "ANALYSIS METHOD SELECT AND DOWNLOAD" and select the "CYANIDE - NO BOUND" program. The system will now call up its operating parameters and set a baseline. Observe this baseline on the instrument screen. If it appears unstable or drifts upward or downward, allow more warm up time for the instrument. Other baseline anomalies may be indicative of other system problems and the operations manual should be referenced and the Department Manager notified.

11.7.7 After the baseline has stabilized, select "SUBMIT" and "CALIBRATE NOW". The system will re-zero the baseline and perform a calibration. The data system will perform a linear least squares regression analysis based on the segments selected. All usable segments must have an R^2 fit of .9950 or better to be deemed acceptable. If the calibration fails to meet this criteria, the system will indicate this and require analyst review of the calibration prior to acceptance. The reason for the calibration failure should be determined and the calibration re-run if necessary.

NOTE: It is recommended that the analyst review the calibration data before running samples, even if the calibration has passed. A good mathematical curve fit might not produce accurate results near the detection limit/baseline, and the curve might necessarily need to be re-run even though the fit was acceptable due to anomalous baseline response.

11.7.8 After the calibration has been passed and accepted by the analyst, select "IDENTIFICATION". Remove the default end run marker (..) by overwriting with two spaces. Escape to exit.

11.7.9 Select "RUN CURRENT TRAY". Follow the instructions to initiate the run using "Y" for start tray, "96" for number of samples, and "1" for tray start position.

11.7.10 The analyzer will run the samples and determine the ammonia concentrations using the newly created calibration curve. For this data to be acceptable, the criteria in Table 3 must be met.

Table 3.
Run Data Acceptance Criteria.

Sample Type	Acceptance Parameter	Action Upon Parameter Failure
Blanks	< Reporting D.L. or <M.D.L (spec case)	Re-analyze blank - if still fails, recalibrate and re-run - if still fails prepare fresh, re-cal and re-run
Old Check Std	± 15 % of known value	Re-analyze check std - if still fails, recalibrate and re-run - if still fails prepare fresh and re-run
New Check Std	± 15 % of known value	Must be within 10 % of old check std, else prepare fresh calibration standards and re-calibrate
High Cal Std	± 15 % of known value	Re-analyze standard - if still fails, recalibrate and re-run - if still fails prepare fresh, re-cal and re-run
Method Blank	< Reporting D.L. or <M.D.L (spec case)	Re-analyze - if contamination is suspected, redigest - if proven, redigest batch if hits
LCS	within established control limits or 80-120	If out of control, re-analyze - if still fails, redigest - if still fails, re-cal - if still fails, redigest set
Matrix Spike	within established control limits and RPD	Evaluate data, **must obtain managerial approval to report**, initiate corrective action
Matrix Spike Duplicate	within established control limits and RPD	Evaluate data, **must obtain managerial approval to report**, initiate corrective action
Sample Results	within 10% of calibration curve high standard	Dilute sample with cal blank solution and re-run
Continuing Check Stds	± 15 % of known value	Correct problem, reanalyze all samples since last good CCV - if fails, re-cal and re-run
Continuing Blanks	< Reporting D.L. or <M.D.L (spec case)	Correct problem, reanalyze all samples since last good CCB - if fails, re-cal and re-run

NOTE: Batch data not within specified limits may be re-analyzed later in the run. The ICB, ICV, and High Calibration Standard must pass to continue with the run. Any dilution factors used on samples are to be noted in the log book and on the run sheet. Samples falling outside the high end of the curve may be diluted with 0.25 N NaOH and re-run.

In addition, if the old versus new check standards fail to meet the above criteria and fresh working standard preparation does not resolve the discrepancy, the stock standards should be re-titrated to verify the cyanide concentration of BOTH calibration and spiking standard. If the concentration has changed, the standards and logs must be updated as if a new preparation had been performed, but using the original expiration date(s).

11.8 CALCULATIONS

After a run has been completed and all of the verification standards are in control, the data may calculated and reported.

For liquids:

$$mg\ CN^-/L = \frac{Lachat\ result \times dilution\ factor \times final\ distillate\ volume\ (mL)}{initial\ sample\ volume\ (mL) \times 1000}$$

For solids:

$$mg\ CN^-/L = \frac{Lachat\ result \times dilution\ factor \times final\ distillate\ volume\ (mL)}{initial\ sample\ weight\ (g) \times 1000}$$

(The dilution factor is 1, unless additional dilution of the sample was done at the instrument.)

For amenable cyanide:

Cyanide amenable to chlorination =

Total cyanide (untreated sample) - Total cyanide (treated sample)

NOTE: The cyanide amanable to chorination test is subject to a matrix interference in the presence of iron-cyanide complexes. If the result of the treated sample is higher than the total cyanide result but is within precision limits for the method, the result should be reported as "no determinable quantities of cyanide amenable to chlorination". If the difference is greater than precision limits, the nature of the interference should be determined and accounted for in the reported result

12.0 MAINTENANCE AND TROUBLESHOOTING

12.1 GENERAL

Glassware should be cleaned appropriately (see Section 4.0) to avoid sample contamination. Equipment should be kept clean and maintained to avoid sample contamination and assure proper operation Manuals supplied by the manufacturers with the instrumentation typically have informational and troubleshooting sections.

12.2 TECHNICAL SUPPORT

Technical support is available from equipment manufacturers (for example, by telephone, fax, or e-mail) They can be used who may be unsure of the instrumentation and a good resource when troubleshooting options have been exhausted Technical support departments can readily supply part numbers.

13.0 REFERENCES

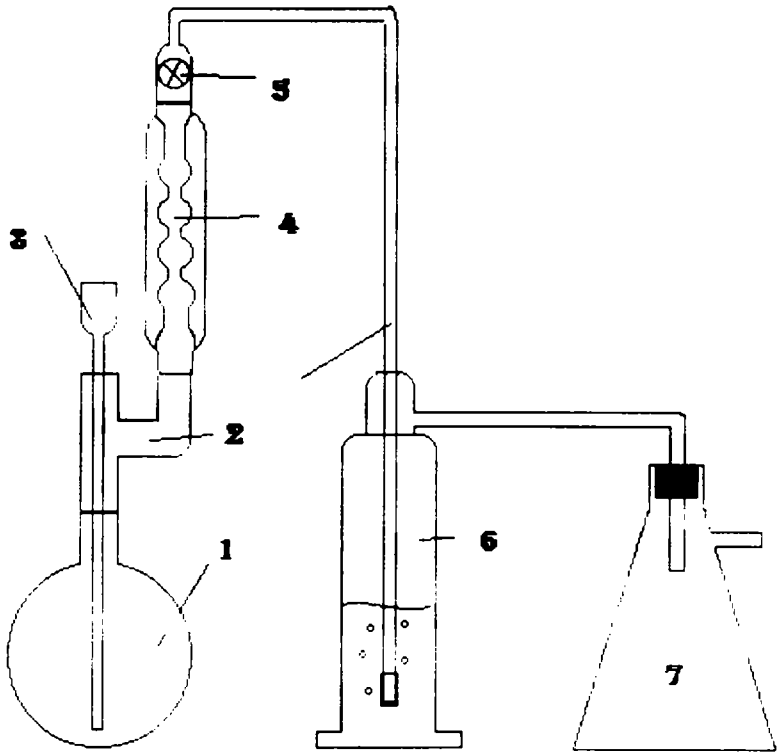
13.1 Method 335.4: Cyanide, Total (Semi-automated colorimetry).
13.2 Methods 4500-CN⁻: A, B, C, E, and G: Standard Methods for the Examination of Water and Wastewater, 18th Edition, 1992.
13.3 Methods SW-846 - 9010B (Revision 2): Total and Amenable Cyanide, Distillation; and 9012A (Revision 1). Total and Amenable Cyanide (Automated Colorimetric, with Off-line Distillation).
13.4 Great Lakes Analytical Quality Assurance Program Manual.
13.5 Great Lakes Analytical Chemical Hygiene Plan.
13.6 Great Lakes Analytical SOP for Login Department
13.7 Great Lakes Analytical SOP for Hazardous Sample Management.

14.0 DEFINITIONS

See References.

Figure 1.

Apparatus for cyanide distillation.



1. 500-mL Round-bottom flask
2. Claissen adapter
3. Thistle top tube funnel
4. Allihn condenser
5. Stopcock/connecting tubing
6. Gas scrubber/absorber
7. Vacuum trap (outlet to vacuum pump)

APPENDIX A.

EXAMPLES OF DOCUMENTATION SHEETS.

A.1 Log book cover page.

A.2 Reagent preparation log sheet - 10.17: Stock calibration/reference standards.

A.3 Reagent preparation log sheet - 10.10: Sulfamic acid solution.

A.4 Reagent preparation log sheet - 10.14: Magnesium chloride solution.

A.5 Reagent preparation log sheet - 10.27 Phosphate buffer solution.

A.6 Reagent preparation log sheet - 10.25: Pyridine-barbituric acid reagent.

A.7 Cyanide determinations run log.

Book nnn

TOTAL CYANIDE

(TOTAL AND AMENABLE CYANIDES)

GLA 335.4 BG

PREPARATION AND ANALYSIS

LOG BOOK

Date Started: _____

Date Stopped: _____

This is a controlled document (properly identified and logged).

QA Manager: _____ Date: _____

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REAGENT PREPARATION LOG SHEET

GLA 335.4 BG CYANIDE: STOCK CALIBRATION/REFERENCE STANDARDS

Preparation of Cyanide Stock Standard Solutions (10.17)					
Weigh ~260 mg of KCN and 0.1-0.2 g NaOH (several pellets) into a 1-L volumetric flask, dissolve in reagent water, dilute to the mark and mix. This solution is approximately 100 ppm CN^-. Label the solution calibration standard "A" or "B" as appropriate. Actual concentrations are determined titrimetrically per Appendix B.					
Reagent	**Weight (g)**	**Manufacturer**	**Lot No.**	**GLA No.**	**Rec'd Date**
KCN "A"					
KCN "B"					
NaOH					
Silver nitrate	**Concentration (N)**				
- #1		Mallinckrodt			
- #2		Ricca			
Analyst/date:					

Titration of Cyanide Stock Standard Solution "A"				
Date	**Initials**	**Silver Nitrate**	**Volume Titrant (mL)**	**Calculated Cyanide (mg/L)**
		#1		
		#2		
Average cyanide concentration =				

GLA Code No.:	Exp. Date.

Titration of Cyanide Stock Standard Solution "B"				
Date	**Initials**	**Silver Nitrate**	**Volume Titrant (mL)**	**Calculated Cyanide (mg/L)**
		#1		
		#2		
Average cyanide concentration =				

GLA Code No	Exp. Date

REAGENT PREPARATION LOG SHEET

GLA 335.4 BG CYANIDE: REAGENTS FOR DISTILLATIONS

Preparation of Sulfamic Acid Solution (10.10)									
Dissolve 40 g of sulfamic acid (H_2NSO_3H) in 1 L of reagent water.									
	Reagent	**Manuf.**	**Lot No.**	**GLA No.**	**Rec'd Date**	**Weight (g)**	**GLA Code No.**	**Expiry**	**Analyst Initals/Date**
1	Sulfamic acid								
2									
3									
4									
5									
6									
7									
8									
9									
10									
11									
12									
13									
14									
15									
16									
17									
18									
19									
20									

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REAGENT PREPARATION LOG SHEET

GLA 335.4 BG CYANIDE: REAGENTS FOR DISTILLATIONS

Preparation of Magnesium Chloride Solution (10.14)									
Dissolve 510 g of magnesium chloride ($MgCl_2$) in 1 L of reagent water.									
	Reagent	**Manuf.**	**Lot No.**	**GLA No.**	**Rec'd Date**	**Weight (g)**	**GLA Code No.**	**Expiry**	**Analyst Initals/Date**
1	$MgCl_2$								
2									
3									
4									
5									
6									
7									
8									
9									
10									
11									
12									
13									
14									
15									
16									
17									
18									
19									
20									

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REAGENT PREPARATION LOG SHEET

GLA 335.4 CYANIDE: REAGENTS FOR DISTILLATIONS

Preparation of Phosphate Buffer Solution (10.27)									
Dissolve 138 g of sodium phosphate dibasic (NaH_2PO_4) in 1 L of reagent water. Store refrigerated.									
	Reagent	**Manuf.**	**Lot No.**	**GLA No.**	**Rec'd Date**	**Weight (g)**	**GLA Code No.**	**Expiry**	**Analyst Initals/Date**
1	NaH_2PO_4								
2									
3									
4									
5									
6									
7									
8									
9									
10									
11									
12									
13									
14									
15									
16									
17									
18									
19									
20									

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REAGENT PREPARATION LOG SHEET

GLA 335.4 CYANIDE: REAGENTS FOR ASSAY

Preparation of Pyridine-Barbituric Acid Reagent (10.25)

Weigh 15 g of barbituric acid (A) into a 1-L reagent bottle. Rinse down the sides and wet with about 100 mL of reagent water. In a fume hood, add 75 mL of pyridine (B), and mix thoroughly. Carefully add 15 mL of concentrated HCl (C) and mix. Transfer to a 1000-mL volumetric flask and dilute to the mark with reagent water. Mix until all of the barbituric acid has dissolved. This solution is stable for six months.

Reagent		Manuf.	Lot No.	GLA No.	Rec'd Date	
A-1	Barbituric acid					
-2						
B-1	Pyridine					
-2						
C-1	conc HCl					
-2						

	Barb. Acid (A)	Weight A (g)	Pyridine (B)	conc. HCl. (C)	GLA Code No.	Expiry	Analyst Initals/Date
1	A-1		B-1	C-1			
2							
3							
4							
5							
6							
7							
8							
9							
10							
11							
12							
13							
14							
15							

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GLA 335.4 CYANIDE RUN LOG

Page n of N

Batch No.:			**Matrix:**		
	Analyst	**Date**	**Spiking/Cal. Standard**	**Conc.**	**Expiry**
Sample Prep.:			GLA-		
Sample Analysis:			GLA-		
Carrier:	**Buffer:**		**Reagent:**	**Chlor-T:**	

	Client GLA Sample ID	Amount used (mL/g)	Dilution Factor	Lachat Reading	Lachat Result	Calculated Result (mg/L CN^-)	Recovery (%)
1	MB						
2	LCS						
3	MS						
4	MSD						
5							
6							
7							
8							
9							
10							
11							
12							
13							
14							
15							
16							
17							
18							
19							
20							
21							
22							
23							
24							

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APPENDIX B.

DETERMINATION OF CYANIDE CONCENTRATIONS BY TITRATION.

B.1 Cyanide in solution forms a complex with added silver ion. After all cyanide becomes bound, excess silver ion is detected by the silver sensitive indicator p-dimethylaminobenzalrhodanine, which changes from a yellow to a salmon color.

B.2 Aliquot 50 mL of the approximately 100 ppm cyanide stock solution to a beaker suitable for titration, add 5 mL of 1.25 N NaOH, a stir bar, and 0.5 mL (10 drops) of indicator solution. Provide moderate stirring.

B.3 Place silver nitrate ($AgNO_3$) titrant #1 into a 10-mL buret, and titrate the diluted cyanide solution to the first change in color from a canary yellow to a salmon hue. Record the volume used.

B.4 Prepare and titrate 5 additional aliquots of cyanide stock standard solution, 2 using titrant #1 and 3 with titrant #2

B.5 Prepare a blank by adding 5 mL of 1.25 N NaOH to 50 mL of reagent water. Add 0.5 mL (10 drops) of indicator solution. Plate on the magnetic stirrer and titrate. Record the volume of titrant used.

B.6 Calculate the concentration of cyanide in the stock standard from each titration by:

$$mg\ CN^-/L = \frac{(A - B) \times normality\ titrant \times 10}{0.0192}$$

Where:
A = volume of titrant used for cyanide stock standard solution.
B = volume of titrant for blank.
10/0.0192 is the conversion factor for normality silver nitrate to mg/L (ppm) cyanide, and accounting for the volume of cyanide stock standard used

B.7 Calculate the average concentration determined.

Standard Operating Procedure for the Digestion of Liquids for the Analysis of Metals

GREAT LAKES ANALYTICAL

STANDARD OPERATING PROCEDURE

FOR

THE DIGESTION OF LIQUIDS FOR THE ANALYSIS OF METALS

GLA 3015 BG

Revision 3.0

Approved By:

Department Manager: _____ Date: 10/1/98

Quality Assurance Manager: _____ Date: 9/19/98

Laboratory Director: _____ Date: _____

1.0 APPLICABILITY

This standard procedure (SOP) provides instructions for the sample handing and digestion of liquids in preparation for analysis of total metals by ICP-OES and FLAA/GFAAS. This SOP is an interpretation of EPA Methods 300.7 and 300.9; Standard Methods no. 3030, Sections E, F, and K; and SW-846 no. 3015 and 3010M. This SOP is to be used in conjunction with the analysts' in-laboratory training, the Great Lakes Analytical Chemical Hygiene Plan (CHP), and the Great Lakes Analytical Quality Assurance Program.

NOTE: The digests produced using this procedure are not suitable for the analysis of mercury (Hg) or hexavalent chromium (Cr^{6+}). Arsenic (As) and selenium (Se) cannot be analyzed by FLAA.

1.1 MATRICES

This method is applicable to aqueous samples (ground, waste, drinking waters), extracts, and other liquid materials and wastes (such as oil and grease)

1.2 REGULATORY APPICABILITY

40 CFR 121

2.0 SUMMARY

A representative 5-100 mL portion of sample is digested with nitric acid, or nitric acid and hydrogen peroxide (for As and Se). The digestate is then refluxed with additional nitric acid (GFAAS methods, except for As and Se) or with hydrochoric acid (ICP-OES methods). Aqueous ground waters, extracts, and liquid samples are digested by either standard "hotplate" digestion methods or microwave-assisted digestion methods. Non-aqueous or high dissolved organic containing liquids are digested using the standard hotplate methods including GLA 3010M, a modified 3010 method. Liquid matrix types include:

- Waters - ground, waste, drinking, other aqueous.
- Extracts - TCLP, SPLP, ASTM D3987-85
- Miscellaneous - oil, grease, diesel, other.

See Appendix A for method exceptions.

3.0 SAFETY

3.1 GENERAL

This SOP does not address all safety issues associated with its use. A reference file of material safety data sheets (MSDS's) is available to all personnel along with the Great Lakes Analytical Chemical Hygiene Plan. Gloves are worn when handling chemicals and reagents.

3.2 CHEMICAL HYGIENE PLAN

The Great Lakes Analytical Chemical Hygiene Plan (CHP) is designed to establish safe work procedures and minimize exposure to hazardous chemicals encountered in the laboratory. The CHP provides information to employees regarding potential hazards and training to minimize these hazards.

3.3 HAZARDOUS SAMPLES

All samples that are received by the laboratory have the possibility of containing hazardous pollutants. They should be treated with caution at all times. Gloves are worn when handling samples. Also see the Great Lakes Analytical SOP for Hazardous Sample Management.

3.4 CHEMICALS SPECIFIC TO DIGESTIONS

30% Hydrogen peroxide is a strong oxidizer in the presence of acids, and can cause burns to eyes and skin. It can react violently when introduced to a sample in concentrated acid. Large volumes of hydrogen gas may be produced. Allow samples to cool thoroughly before adding hydrogen peroxide. Similarly, add concentrated nitric acid to samples carefully.

4.0 INTERFERENCES

4.1 Sample matrices can vary greatly, even within specific sample type groups, most notably waste sludges (for example, ground water versus tank removal waste). Any sample types exhibiting significantly different properties, such as high organic content or multi-phase samples, are to be handled as individual matrices, and appropriate matrix spikes should be produced and analyzed.

4.2 In the case of methods for total recoverable and/or dissolved metals, digestion is not always required. It should be noted, however, that the less intensive digestion procedure for total recoverable metals may not be sufficiently vigorous to destroy some metal complexes and may therefore give biased results.

4.3 Daily monitoring test of the deionized water supply must have been performed and pass or meet appropriate criteria for analysis before the water can be used in sample preparation. All glassware to be used in the analysis must be cleaned and rinsed following the procedure outlined in Appendix C. Periodic cleaning of sample preparation and analysis areas, will be performed. At least quarterly, laboratory dust wipes will be prepared and analyzed. Contamination of more than 500 ug of lead (Pb) per square foot is not permitted.

5.0 RECORD KEEPING

5.1 Each analyst is responsible for keeping accurate and up-to-date records of all digestions performed.

5.2 Digestion Log Book:

A log book will be maintained for all solid matrix types and associated digestions. All information regarding samples processed in the lab will be entered into this book. This information will include but is not limited to:

- Method reference number
- Client Name for each set of samples
- GLA Sample ID (one complete for each set)
- Initial sample volume used
- LIMS batch reference number
- Analyst's signature and date prepared/analyzed
- Reviewer's signature and date
- All readings, dilution factors, and calculated results
- Sample matrix type
- Spiking volumes used
- Spike standard identifier
- Spike standard concentration
- LCS and matrix spike information
- Final digestate volume

This log should also include any unique observations noted in regard to specific samples. Space will be reserved on each page for calculations and notes. All unused portions of logbook pages must be z'ed out.

5.3 Sample Schedule - All samples will be tracked through the lab using GLA sample I.D. numbers generated by the GLA LIMS system.

6.0 QUALITY CONTROL

6.1 QUALITY CONTROL SAMPLES

Quality control samples are run at a minimum 5% frequency (*i.e.* one set with every batch of twenty or less samples). The results of these samples are used to gauge accuracy and precision of the method. These samples include method blanks (MB), lab control samples (LCS), matrix spikes (MS) and matrix spike duplicates (MSD). The quality control samples contain all reagents and are subjected to all preparation steps. They are processed and analyzed along with test samples.

6.2 METHOD BLANK

Matrix-matched method blanks (MB) containing all reagents and subjected to all preparation steps are processed and analyzed along with the samples. Method blanks must produce a concentration below the reporting limit (*e.g.* PQL, EQL, .) for an analytical batch to be valid. These samples provide a measure of laboratory and/or reagent contamination. Test sample results are not corrected for the method blank concentrations.

6.3 LABORATORY CONTROL SAMPLE (LCS)

An external (independently sourced) reference standard is prepared within the working range of the method and analyzed with each matrix per batch of twenty or less samples (*i.e.* minimum 5% frequency). The results of the samples must be within established control limits, or where there is not enough data to calculate control limits, within 15% of the known value.

6.4 MATRIX SPIKED SAMPLES

Matrix spiked samples (MS and MSD) will be analyzed with a minimum frequency of 5% (*e.g.* one set per 20 or less samples per matrix) and are used to determine accuracy and precision of a method. The matrix spiked samples will be spiked using the same standards used to spike the LCS samples. The analyzed result of the matrix spikes must be within established control limits or where there is not enough data to calculate control limits, within 25% of the known value.

6.5 SURROGATE MATRIX BLANK AND SPIKED SAMPLES

In cases where no additional sample is available for matrix spiking (*e.g.* wipes samples), a set of surrogate matrix QC samples will be produced by digesting an appropriate substrate "blank" and two spiked samples of the same substrate spiked with the same standards and at the same levels of the LCS.

6.6 QUALITY CONTROL TRACKING AND DATA REVIEW

The QC data is considered acceptable and actual sample results can be evaluated and reported by the analyst if all QC samples are within established control limits.

6.7 CORRECTIVE ACTION

If a quality control measure fails, corrective action is taken and documented to ensure the accuracy of the data that is reported. Examples of when corrective action sheets are filled out are:

- A sample or QC is re-analyzed. This may be due to the QC parameter failing or mislabeling of samples.
- Samples are reported with a QC result (blank, spike matrix) parameter out of control. In this case, not only should a corrective action be initiated, but the data must be flagged
- A deviation from the normal SOP for the method is discovered (*e.g* a digestion goes down to dryness or a different concentration of reagent is used) and the sample is analyzed and reported.
- An error in a previously reported sample is discovered.

7.0 SAMPLE MANAGEMENT

7.1 The procedure for sample management are detailed in the Great Lakes Analytical SOP for sample receipt into the laboratory.

7.2 Sample Schedule. Analysts keep track of sample throughput by using the Laboratory Information Management System (LIMS). The system is checked daily and a hard copy generated. Samples for this method are queued under "METP". The information includes:

- Client name.
- Sample numbers.
- Project name.
- Matrix.
- Hold time and turnaround time.

8.0 METHOD VALIDATION

8.1 QUALITY CONTROL BOOK

Method validation must be performed before any actual samples can be analyzed. Method validation studies are required to be stored in the QC logbook. Method exception studies must also be performed to validate any exception taken by proving equivalency with the unaltered method The contents of the QC book include:

- Copy of the GLA Quality Assurance Program.
- Copies of GLA SOP and source methods.
- Copy of the precision and accuracy study for the method
- Copies of all method detection limit studies and dates in use.
- Check standard recovery tabulations and control limits.
- Spike and spike duplicate recovery tabulations and control limits.
- Corrective action sheets.

8.2 QUALITY ASSURANCE PROGRAM

Internal audits will be performed periodically to assess analytical system performance Performance evaluation samples will be analyzed periodically to assess laboratory performance. (Refer to the GLA Quality Assurance Program)

8.3 METHOD DETECTION LIMIT STUDY

8.3.1 The method detection limit (MDL) is defined as the minimum concentration of analyte that can be determined with 99% confidence. It is determined as follows:

- Prepare a minimum of seven replicate samples at a concentration at or near the expected MDL. Carry these replicates through the entire sample preparation procedure and analysis.
- Calculate the MDL by taking the standard deviation of the results of the seven replicates and multiply by the Student's t value at n-1 degrees of freedom (3.143 for seven replicates).

8.3.2 Other factors such as matrix effects and instrument noise may affect the attainable detection limit. These should be quantified if possible and taken in to account when determining an MDL as the obtainable detection level may be artificially elevated due to these factors

8.3.3 A new MDL study must be performed to re-evaluate the method if any major instrument maintenance or service is performed, if any new method exceptions or changes are made or at least annually.

9.0 EQUIPMENT

9.1 Beakers, Griffin type 250-mL size.
9.2 Watch covers ribbed, 90-mm diameter.
9.3 Volumetric flasks, 25-100 mL.
9.4 Glass funnels.
9.5 Filter paper - 15 cm, Whatman 41, or equivalent.
9.6 Sample containers, 50-100 mL capacity, metal-free.
9.7 Hotplate, adjustable, capable of maintaining a constant temperature for samples of 90-95°C. Monitor temperature of the hotplate by placing an Erlenmeyer flask with approximately 100 mL of cooking oil at the center of the hotplate, and reading the temperature with an ASTM thermometer positioned with the bulb against the bottom of the flask The temperature must be at least 140°C. Record temperatures in the log book.
9.8 Analytical balance, calibrated - capable of weighing to nearest 0.1 g for soil/sediment/sludge samples, 0.001 g for paints.
9.9 Microwave digestion apparatus:

- Microwave digestion system, capable of monitoring and maintaining 175°C and/or 70 p s i within digestion vessels. CEM model MDS-2100, or equivalent
- Lined (polyolefin) digestion vessels 50-mL size.
- Rupture membranes.

10.0 STANDARDS AND REAGENTS

10.1 Reagent water - ASTM Type II Water (DI water)
10.2 Nitric acid - concentrated HNO_3, ACS/reagent grade. Fisher no. A509. **CAUTION:** Nitric acid is corrosive.
10.3 Hydrochloric acid - concentrated HCl, ACS/analytical reagent grade. Fisher no A508. **CAUTION:** Hydrochloric acid is corrosive.
10.4 Hydrogen peroxide - 30% H_2O_2, ACS/analytical reagent grade. Fisher no H325
10.5 Spiking standards - GLA-SPK-1A, -3B, 5, and 6 Inorganic Ventures; GLA-SPK-EM (earth metals spike) prepared from individual 10,000 ppm solutions (from Inorganic Ventures) for final concentrations of 2000 ppm of Na, K, Ca, and Mg. (Refer to Appendix B for concentrations and volumes spiked.)

11.0 PROCEDURE

NOTE: Method validation (section 8.0) must be performed before samples can be analyzed.

11.1 SELECTION OF DIGESTION PROCEDURE

The appropriate method for the required metal analysis must be referenced in order to select the proper digestion procedure. There are several methods for digestions which can be selected based upon the matrix type of the sample and the type of digestion being performed. Use Table 1 to determine which method is most applicable to the samples being analyzed. The proper digestion procedure is selected from Table 2

Table 1.
Digestion Method Reference Chart.

Analysis	Method Reference	Pre-Digestion Preparation	Microwave Digestions	Standard Digestions			Special Matrices
				ICP/FLAA	GFAA	Special	
Total Metals	SW-846	Preserve with HNO_3 to pH <2	3051A	3010A	3020A	7060A (As) 7740A (se)	3010M for oils, gas, diesel, and waste oil sludges
	EPA		n/a	4.1.3 200.7	4.1.3 200.9	206.2 (As) 270.2 (se)	
	Std Meth		SM-3030-K	SM-3030-F	SM-3030-E		
Dissolved Metals	SW-846	Filter thru 0.45 µ filter, preserve with HNO_3 to pH <2	3015	3010A	3020A	7060A (As) 7740A (Se)	**3010M for oils, gas, diesel, and waste oil sludges**
	EPA		n/a	4.4.1/4.1.3 200.7	4.1.1/4.1.3 200.9	206.2 (As) 270.2 (Se)	
	Std Meth		SM-3030-K	SM-3030-F	SM3030-E		
Total Recoverable Metals	SW-846	Preserve with HNO_3 to pH <2	n/a	3005	n/a		3005
	EPA		n/a	4.1.4	4.4.4		4.1.4
	Std Meth		n/a	SM-3030-F	SM-3030-F		SM-3030-F

11.2 Assemble all materials and equipment required for the procedure. A daily calibration check of the analytical balance must have been performed prior to its use in weighing samples or standard materials. Record all pertinent sample information in the log book(s) ***before beginning the analysis***.

CAUTION: All hotplate digestions must be performed in a fume hood

Table 2.
Procedure Selection Table.

Digestion Type	Analysis Type (1)	Analysis Method	Applicable Method(s)	Digestion Procedure
Microwave	Total Metals Dissolved Metals	Any (2)	SW-846 3015 SM-3030-K	11.4 (MIC)
Standard	Total Metals Dissolved Metals	ICP/FLAA	SW-846 3010A EPA 4 1 3 EPA 200.7 SM-3030-F	11.5 (ICP)
Standard	Total/Dissolved Except As and Se	GFAAS	SW-846 3020A EPA 4.1.3 EPA 200 9 SM-3030-E	11.6 (GF)
Standard	Total/Dissolved As and Se Only	GFAAS	SW-846 7060A (As) SW-846 7740A (Se) EPA 206.2 (As) EPA 270.2 (Se)	11.7 (AS)
Standard	Total Metals	Any (2)	3010M (3)	11.8 (NA)
Standard	Total Recoverable Metals	ICP/FLAA	SW-846 3005 EPA 4.1 4 SM-3030-F	11.9 (A)

(1) Dissolved metals require filtration at time of collection (through a 0.45 u membrane filter) **prior to preservation**. Chain of custody record should be referenced to determine if sample was properly collected, filtered, and preserved.
(2) Any analytical method refers to GLA routine methods : ICP, GFAAS, and FLAA. These digests are not suitable for analysis of mercury or hexavalent chromium.
(3) Method 3010M is a GLA method. It is based upon the SW-846 method 3010A, but the addition of hydrochloric acid has been omitted. It is used exclusively for the analysis of metals in oils, oil waste, gas, diesel fuels, and high organic containing waters.

11.3 PREPARATION OF QUALITY CONTROL AND TEST SAMPLES

11.3 1 Method blank - Aliquot 100 mL (45 mL for microwave digestion section 11 4) of reagent water into a clean digestion vessel.

11.3 2 Laboratory control samples (LCS) - Aliquot 100 mL (45 mL for microwave digestion, section 11 4) of reagent water into a clean digestion vessel. Accurately aliquot 0 2 mL (0 1 for microwave) each of GLA-SPK-1A, -3B, -5, and -EM into the sample. Also add 0.2 mL (0.1 for microwave) of GLA-SPK-6 if spiking Ag and Cd at ICP levels.

11 3.3 Samples - Representative 100 mL (45 mL for microwave digestion, section 11.4) aliquots of samples are aliquoted into clean digestion vessels. For samples with a high solids content (> 1%), a smaller sample size should be used (record the actual volume in the log book)

11 3.4 Matrix spike samples - Measure two additional aliquots 100 mL (45 mL for microwave digestion section 11 4) of one sample, with volumes similar to the test sample volume, and making sure each aliquot is homogeneous and representative of the entire sample. Accurately aliquot 0 2 mL each of GLA-SPK-1A, 3B, -5, and -EM into the sample. Also add 0 2 mL (0.1 for microwave) of GLA-SPK-6 if spiking Ag and Cd at ICP levels. Mark as MS and MSD.

11.4 MICROWAVE-ASSISTED DIGESTION OF AQUEOUS LIQUIDS AND EXTRACTS (MIC)

NOTE: Metal analytes for which this digestion is applicable include:
Ag, Al, As, Ba, Be, Cd, Ca, Cr (tot), Co, Cu, Fe, Pb, Mg, Mn, Mo, Ni, K, Na, Sb, Se, Tl, V, Zn.

11.4.1 Add 5 mL of concentrated HNO_3 to each sample. Stand for 2-10 minutes to allow any vigorous reaction to occur before the vessel is sealed.

11.4.2 The "control vessel" should be selected as the sample appearing to be most reactive. Load the carousel with samples and place in the microwave.

11.4.3 Upon completion of the microwave program, the samples are cooled until the pressure drops below 10 psi (as indicated by the instrument). The pressure sensor is carefully disconnected, temperature probe removed, and the carousel taken out of the instrument.

11.4.4 Each vessel is carefully vented, vent line removed, cap retightened, and shaken to mix.

11.4.5 Each vessel is opened and contents poured into a clean labelled sample cup. If the sample is still warm, or hot, to the touch, it should be cooled further and mixed before analysis. This can be expedited by placing samples in a refrigerator, freezer, or cold water bath for a short time. Observe the volume of each vessel. If loss of sample is apparent (*e.g.* volume less than 50 mL), the sample is discarded and redigested. The container should be labeled with:

- GLA Sample I.D.
- Matrix type
- Date digested
- Dilution factor (where applicable)

11.4.6 Samples are now ready for analysis by ICP, GFAA, or FLAA.

11.5 HOTPLATE DIGESTION OF AQUEOUS LIQUIDS AND EXTRACTS FOR ANALYSIS BY ICP-OES (ICP)

NOTE: Metal analytes for which this digestion is applicable include:
Al, Ba, Be, Cd, Ca, Cr (tot), Co, Cu, Fe, Pb, Mg, Mn, Mo, Ni, K, Na, Tl, V and Zn.

11.5.1 Add 3 mL of concentrated HNO_3, and several boiling chips to each sample, cover with watch glasses, and mix.

11.5.2 Place on a hotplate and maintain at 90-95°C until the volume has been reduced to approximately 5-10 mL. Remove and cool.

11.5.3 Add an additional 3 mL of concentrated HNO_3 to each sample, cover, and return to the hotplate for 20 minutes, or until the digestion is complete. Allow the volume to reduce to 5-10 mL. Remove and cool.

11.5.4 Add 5 mL of reagent water and 5 mL of concentrated HCl to each sample, cover, and return to the hotplate for 15 minutes. Remove and cool.

11.5.5 Rinse down the watchglass and sides of the beakers. If necessary, filter the digestate through a Whatman 41 filter paper into a clean 100-mL volumetric flask, dilute to the mark with reagent water, mix and transfer to a metal-free container. The container should be labeled with:

- GLA Sample I.D.
- Matrix type
- Date digested
- Dilution factor (where applicable)

11.5.6 The samples are ready for analysis by ICP (or FLAA).

11.6 DIGESTION OF AQUEOUS LIQUIDS AND EXTRACTS FOR ANALYSIS BY GFAA (GF)

NOTE: Metal analytes for which this digestion is applicable include: **Be, Cd, Cr (tot), Pb, Mo, Tl, and V.**

11.6.1 Add 3 mL of concentrated HNO_3, and several boiling chips to each sample, cover with watch glasses, and mix.

11.6.2 Place on a hotplate and maintain at 90-95°C until the volume has been reduced to approximately 5-10 mL. Remove and cool.

11.6.3 Add an additional 3 mL of concentrated HNO_3 to each sample, cover, and return to the hotplate for 20 minutes or until the digestion is complete. Allow the volume to reduce to 5-10 mL. Remove and cool.

11.6.4 Add 10 mL of reagent water, cover, and return to the hotplate for 15 minutes. Remove and cool.

11.6.5 Rinse down the watchglass and sides of the beakers. If necessary, filter the digestate through a Whatman 41 filter paper into a clean 100-mL volumetric flask, dilute to the mark with reagent water, mix, and transfer to a metal-free container. The container should be labeled with:

- GLA Sample I.D.
- Matrix type
- Date digested
- Dilution factor (where applicable)

11.6.6 The samples are ready for analysis by GFAAS

11.7 DIGESTION OF AQUEOUS LIQUIDS AND EXTRACTS FOR ANALYSIS OF As AND Se ONLY BY GFAA (AS)

NOTE: This digestion is applicable only for analysis of arsenic (As) and selenium (Se) by GFAAS.

11.7.1 Add 1 mL of concentrated HNO_3, 2 mL of 30% hydrogen peroxide, and several boiling chips to each sample, cover with watch glasses, and mix.

11.7.2 Place on a hotplate and maintain at 90-95°C until the volume has been reduced to approximately 50 mL. Remove and cool.

11.7.3 Rinse down the watchglass and sides of the beakers. If necessary, filter the digestate through a Whatman 41 filter paper into a clean 100-mL volumetric flask, dilute to the mark with reagent water, mix, and transfer to a metal-free container. The container should be labeled with:

- GLA Sample I.D.
- Matrix type
- Date digested
- Dilution factor (where applicable)

11.7.4 The samples are ready for analysis by GFAAS (for As and Se).

11.8 HOTPLATE DIGESTION OF NON-AQUEOUS AND MULTI-PHASE LIQUIDS FOR ANALYSIS BY ICP, GFAA, OR FLAA (NA) - METHOD 3010M

NOTE: Metal analytes for which this digestion is applicable include:
Ag, Al, As, Ba, Be, Cd, Ca, Cr (tot), Co, Cu, Fe, Pb, Mg, Mn, Mo, Ni, K, Sb, Se, Na, Tl, V, and Zn.

11.8.1 Add 5 mL of concentrated HNO_3, and several boiling chips to each sample, cover with watch glasses, and mix.

11.8.2 Place on a hotplate and maintain at 90-95°C for 15 minutes, or until the volume has been reduced to approximately 10 mL. Remove and cool.

11.8.3 Add an additional 5 mL of concentrated HNO_3 to each sample, cover, and return to the hotplate for 30 minutes, or until the digestion is complete. Allow the volume to reduce to 5-10 mL. Remove and cool. Add an additional 5 mL of concentrated HNO_3, cover, and heat for an another 30 minutes. Allow the volume to reduce to 5-10 mL. Remove and cool.

11.8.4 Add 2 mL of reagent water and 3 mL of 30% hydrogen peroxide to each sample, cover, and return to the hotplate for 15 minutes. Remove and cool.

11.8.5 Rinse down the watchglass and sides of the beakers. Filter the digestate through a Whatman 41 filter paper into a clean 100-mL volumetric flask, dilute to the mark with reagent water, mix, and transfer to a metal-free container. The container should be labeled with:

- GLA Sample I.D.
- Matrix type
- Date digested
- Dilution factor (where applicable)

11.8.6 The samples are ready for analysis by ICP/GFAA/FLAA.

11.9 HOTPLATE DIGESTION OF AQUEOUS AND NON-AQUEOUS LIQUIDS FOR ANALYSIS OF TOTAL RECOVERABLE METALS BY ICP, GFAA, OR FLAA (A)

NOTE: Metal analytes for which this digestion is applicable include:
Ag, Al, As, Ba, Be, Cd, Ca, Cr (tot), Co, Cu, Fe, Pb, Mg, Mn, Mo, Ni, K, Sb, Se, Na, Tl, V, and Zn.

11.9.1 Add 2 mL of concentrated HNO_3, 5 mL of concentrated HCl, and several boiling chips to each sample, cover with watch glasses, and mix.

11.9.2 Place on a hotplate and maintain at 90-95°C until the volume has been reduced to approximately 5-10 mL. **Do not boil samples!** Remove and cool.

11.9.3 Rinse down the watchglass and sides of the beakers. Filter the digestate through a Whatman 41 filter paper into a clean 100-mL volumetric flask, dilute to the mark with reagent water, mix, and transfer to a metal-free container. The container should be labeled with:

- GLA Sample I.D.
- Matrix type
- Date digested
- Dilution factor (where applicable)

11.9.4 The samples are ready for analysis by ICP/GFAA/FLAA.

12.0 MAINTENANCE AND TROUBLESHOOTING

12.1 GENERAL

Glassware should be cleaned appropriately to avoid sample contamination. Equipment should be kept clean and maintained to avoid sample contamination and assure proper operation Manuals supplied by the manufacturers with the instrumentation typically have informational and troubleshooting sections.

12.2 TECHNICAL SUPPORT

Technical support is available from equipment manufacturers (for example, by telephone, fax, or e-mail). They can be a good resource when troubleshooting options have been exhausted. Technical support departments can readily supply part numbers.

13.0 REFERENCES

13.1 EPA Method 200.7: Inductively Coupled Plasma - Atomic Emission Spectrophotometric Method for Trace Element Analysis of Water and Wastes.
13.2 EPA Method 200.9: Determination of Trace Elements by Stabilized Temperature Graphite Furnace Atomic Absorption Spectrometry.
13.3 Method 3030 Preliminary Treatment of Samples, Sections E (Nitric Acid Digestion), F (Nitric Acid-Hydrochloric Acid Digestion), and K (Microwave-Assisted Digestion). Standard Methods for the Examination of Water and Wastewater, 18th Edition, 1992.
13.4 Method SW-846, 3050B: Acid Digestion of Sediments, Sludges, and Soils
13.5 Great Lakes Analytical Quality Assurance Program.
13.6 Great Lakes Analytical Chemical Hygiene Plan.
13.7 Great Lakes Analytical SOP for Login Department.
13.8 Great Lakes Analytical SOP for Hazardous Sample Management.

14.0 DEFINITIONS

See References.

APPENDIX A.

METHOD EXCEPTIONS.

A.1 Section 1.0 - Sample Preservation

EPA 200 Series, section 4 1.4:

- Amounts of nitric and hydrochloric acids added to the preserved sample are in accordance with SW-846 Method 3005.

SM-3030-F.

- Amounts of nitric and hydrochloric acids added to the preserved sample are in accordance with SW-846 Method 3005

A.2 Section 11.5 (ICP)

EPA Method 200.7:

- Section 11.2.3 - Acid concentrations are made in accordance with SW-846 3010A. The higher concentrations of acid will not compromise the digestion process.
- Sections 11.2.2-11.2.6 - Pre-concentration of samples is not performed unless detection levels are required that are below those attainable by current analytical procedures.

SM-3030-F:

- Additions of acid are made in accordance with SW-846 3010B The higher concentrations of acid will not compromise the digestion process

A.3 Section 11.6 (GF)

EPA Method 200.9:

- Section 11.3.3 -The addition of hydrochloric acid in step 11.3.3 has been omitted, and an additional additions of nitric acid are made in its place. The interferences associated with chloride in graphite furnace analysis are well documented (for example, in EPA 200 Series, section 4 1.3)
- Sections 11.2.2-11.2.6 - Pre-concentration of samples is not performed unless detection levels are required that are below those attainable by current analytical procedures.

SM-3030-E.

- Additions of acid are made in accordance with SW-846 3010B. The higher concentrations of acid will not compromise the digestion process.

A.4 Section 11.7 (AS)

SW-846 Methods 7060A and 7740A:

- The digestates are not pre-mixed with nickel nitrate modifier. The modifier is added to the sampler by the instrument autosampler at the time of analysis

EPA 200 Series Methods 206.2 and 270.2:

- The digestates are not pre-mixed with nickel nitrate modifier The modifier is added to the sampler by the instrument autosampler at the time of analysis

A.5 Section 11.8 (NA)

Modified SW-846 Method 3010A (GLA Method 3010M):

- This method parallels SW-846 Method 3010A. The addition of hydrochloric acid has been replaced by addition of 3 mL of nitric acid. This method is used exclusively for the digestion of gasoline, diesel, oil, and oil sludge waste samples, and aqueous samples with a high organic content. These materials show a wide variance of analyte levels and these digestates are analyzed by ICP, GFAAS, or FLAA.
- For non-aqueous or multi-phase samples, a 5-25 g sample is taken, depending upon organic content and allowable regulatory detection levels required. This dilution factor is included in the final calculations of analyte concentrations.

APPENDIX B.

STANDARD SPIKING LEVELS AND VOLUMES.

Standard	Aliquot/Volume	Aliquot/Volume	Aliquot/Volume	Aliquot/Volume	Aliquot/Volume
GLA-SPK-1A	0.10/100		0.05/50	0.10/50	0.10/50
GLA-SPK-3B		0.05/50		0.10/50	0.10/50
GLA-SPK-4B	0.10/100				
GLA-SPK-5			0.05/50	0.10/50	0.10/50
GLA-SPK-6					0 10/50
EARTH	0 10/100		0.05/50	0 05/50	

Set	Element	Soil	D H_2O FNC	D H_2O ICP	H_2O	TCLP/SPLP Ext.
R C R A	Ag	1.0	0.005		0.01	0.51
	As	0.03	0.015		0.03	0.03
	Ba	1 0		0 50	1 0	1 0
	Cd	1.0	0.001		0.002	0.502
	Cr	1.0	0.003	0.50	1.006	1.006
	Hg		0.001		0.002	0.002
	Pb	1.0	0.015		0.03	0.03
	Se	0.03	0.015		0.03	0.03
P R I R T Y	Be	1.0		0.50	1.0	1.0
	Cu	1.0	0.015	0 50	1.03	1.03
	Ni	1.0		0.50	1.0	1.0
	Sb	1.0	0.015	1 0	2.03	2.03
	Tl	2.0	0.015	1 0	2 03	2 03
	Zn	1.0		0.50	1.0	1 0
T A L	Al	1.0		0 5	1.0	1 0
	Co	1.0		0 5	1.0	1.0
	Fe	1.0		0 5	1 0	1 0
	Mn	1.0		0 5	1.0	1 0
	V	1 0		0 5	1.0	1 0
E A R T H	Ca	1.0		1 0	1.0	
	K	1.0		1.0	1.0	
	Li	1.0		1.0	1.0	
	Na	1.0		1.0	1 0	
	Mg	1.0		1.0	1 0	
E X T R A	B	1.0		1.0	2.0	2.0
	Mo	1.0		1 0	2 0	2.0
	Si	1 0		1.0	2.0	2.0
	Sn	1.0		1 0	2.0	2.0
	Ti	1 0		1 0	2 0	2 0

APPENDIX C.

METALS GLASSWARE PREPARATION

All glassware to be used in the preparation of solutions for metals analysis will be prepared according to the following procedure:

1. All beakers, funnels, flasks, stoppers and watch covers will be examined for gross contamination and soil removal.

2. Any analyst processing glassware through the laboratory dishwasher will use the appropriate detergent supplied.

3. All glassware shall subsequently be *hand-washed* using Neutrad soap (anionic detergent) and triple rinsed with tap water, then triple rinsed with de-ionized water, paying special attention to any glassware unduely etched, cracked or otherwise likely break and/or cause contamination of samples.

4. All glassware which will come into contact with samples to be analyzed for metals will be rinsed with a 50% Nitric Acid solution and triple rinsed with de-ionized water immediately prior to use. Glassware to be used for other inorganic analyses should be rinsed with an acid appropriate to the test. (e.g. - dilute sulfuric for nitrate/nitrite) and triple rinsed with de-ionized water.

Standard Operating Procedure for the Digestion of Solids for the Analysis of Metals

GREAT LAKES ANALYTICAL

STANDARD OPERATING PROCEDURE

FOR

THE DIGESTION OF SOLIDS FOR THE ANALYSIS OF METALS

GLA 3050 BG

Revision 3.0

Approved By:

Department Manager: _____ Date: 10/1/98

Quality Assurance Manager: _____ Date: 9/17/98

Laboratory Director: _____ Date: _____

1.0 APPLICABILITY

This standard procedure (SOP) provides instructions for the sample handing and digestion of solids in preparation for analysis of total metals by ICP-OES and FLAA/GFAAS. This SOP is an interpretation of EPA Methods 300.7 and 300.9; Standard Methods no. 3030, Sections E, F, and K; and SW-846 no. 3050B. This SOP is to be used in conjunction with the analysts' in-laboratory training, the Great Lakes Analytical Chemical Hygiene Plan (CHP), and the Great Lakes Analytical Quality Assurance Program.

NOTE: The digests produced using this procedure are not suitable for the analysis of mercury (Hg) or hexavalent chromium (Cr^{6+}).

1.1 MATRICES

This method is applicable to soils, solids (such as wipes and paints), sediments, and sludges. This method is a very strong acid digestion that will dissolve almost all elements; however, silicate structures are not normally dissolved.

1.2 REGULATORY APPICABILITY

40 CFR 121

2.0 SUMMARY

A representative portion of sample is digested with nitric acid and hydrogen peroxide, and then refluxed with additional nitric (for SW-846 method 3050B) or nitric/hydrochoric acids (EPA method 200.7). The digestate is then filtered and diluted for analysis by ICP, GFAAS, and/or FLAA. A separate sample is dried if necessary for dry weight calculations. Solid matrix types and amounts used include:

- Soils and sediments - 1-2 g portion.
- Paint chips - up to 2 g.
- Paint or dust wipes and filters - entire wipe or filter (including washings).
- Waste sludges - a larger portion may be taken based upon the dry weight, up to 2 g of solid
- Miscellaneous - mixed solids, waste oil sludges (may require particle size reduction and sub-sampling).

The approximate linear upper ranges for a 2-g sample size are:

- As, Be, Cd, Co, Cr, Cu, Mo, Ni, Se, Tl, V, Zn - 1,000,000 mg/kg.
- Pb, Sb - 200,000 mg/kg.
- Ag, Ba - 2500 mg/kg.

Smaller sample sizes should be taken if limits are exceeded

See Appendix A for method exceptions.

3.0 SAFETY

3.1 GENERAL

This SOP does not address all safety issues associated with its use. A reference file of material safety data sheets (MSDS's) is available to all personnel, along with the Great Lakes Analytical Chemical Hygiene Plan. Gloves are worn when handling chemicals and reagents

3.2 CHEMICAL HYGIENE PLAN

The Great Lakes Analytical Chemical Hygiene Plan (CHP) is designed to establish safe work procedures and minimize exposure to hazardous chemicals encountered in the laboratory. The CHP provides information to employees regarding potential hazards and training to minimize these hazards.

3.3 HAZARDOUS SAMPLES

All samples that are received by the laboratory have the possibility of containing hazardous pollutants. They should be treated with caution at all times. Gloves are worn when handling samples Also see the Great Lakes Analytical SOP for Hazardous Sample Management.

3.4 CHEMICALS SPECIFIC TO DIGESTIONS

30% Hydrogen peroxide is a strong oxidizer in the presence of acids. and can cause burns to eyes and skin. It can react violently when introduced to a sample in concentrated acid. Large volumes of hydrogen gas may be produced. Allow samples to cool thoroughly before adding hydrogen peroxide. Similarly, add concentrated nitric acid to samples carefully.

4.0 INTERFERENCES

4.1 Sample matrices can vary greatly, even within specific sample type groups, most notably waste sludges (for example, soil versus water treatment waste sludge). Any sample types exhibiting significantly different properties, such as high organic content or multi-phase samples, are to be handled as individual matrices, and appropriate matrix spikes should be produced and analyzed.

4.2 Daily monitoring test of the deionized water supply must have been performed and pass or meet appropriate criteria for analysis before the water can be used in sample preparation. All glassware to be used in the analysis must be cleaned and rinsed following the procedure outlined in Appendix C. Periodic cleaning of sample preparation and analysis areas, will be performed

5.0 RECORD KEEPING

5.1 Each analyst is responsible for keeping accurate and up-to-date records of all digestions performed.

5.2 Digestion Log Book:

A log book will be maintained for all solid matrix types and associated digestions. All information regarding samples processed in the lab will be entered into this book. This information will include but is not limited to:

- Method reference number
- Client Name for each set of samples
- GLA Sample I.D. (one complete for each set)
- Initial sample weight used
- LIMS batch reference number
- Analyst's signature and date prepared/analyzed
- Reviewer s signature and date
- All readings. dilution factors, and calculated results
- Sample matrix type
- Spiking volumes used
- Spike standard identifier
- Spike standard concentration
- LCS and matrix spike information
- Final digestate volume

This log should also include any unique observations noted in regard to specific samples. Space will be reserved on each page for calculations and notes. All unused portions of logbook pages must be z'ed out.

5.3 Sample Schedule - All samples will be tracked through the lab using GLA sample I.D. numbers generated by the GLA LIMS system.

6.0 QUALITY CONTROL

6.1 QUALITY CONTROL SAMPLES

Quality control samples are run at a minimum 5% frequency (*i.e.* one set with every batch of twenty or less samples). The results of these samples are used to gauge accuracy and precision of the method. These samples include method blanks (MB), lab control samples (LCS), matrix spikes (MS) and matrix spike duplicates (MSD). The quality control samples contain all reagents and are subjected to all preparation steps. They are processed and analyzed along with test samples

6.2 METHOD BLANK

Matrix-matched method blanks (MB) containing all reagents and subjected to all preparation steps are processed and analyzed along with the samples. Method blanks must produce a concentration below the reporting limit (*e.g* PQL, EQL, ...) for an analytical batch to be valid. These samples provide a measure of laboratory and/or reagent contamination. Test sample results are not corrected for the method blank concentrations.

6.3 LABORATORY CONTROL SAMPLE (LCS)

An external (independently sourced) reference standard is prepared within the working range of the method and analyzed with each matrix per batch of twenty or less samples (*i.e.* minimum 5% frequency) The results of the samples must be within established control limits, or where there is not enough data to calculate control limits, within 15% of the known value.

6.4 MATRIX SPIKED SAMPLES

Matrix spiked samples (MS and MSD) will be analyzed with a minimum frequency of 5% (*e.g.* one set per 20 or less samples per matrix) and are used to determine accuracy and precision of a method. The matrix spiked samples will be spiked using the same standards used to spike the LCS samples. The analyzed result of the matrix spikes must be within established control limits, or where there is not enough data to calculate control limits, within 25% of the known value.

6.5 SURROGATE MATRIX BLANK AND SPIKED SAMPLES

In cases where no additional sample is available for matrix spiking (*e.g.* wipes samples), a set of surrogate matrix QC samples will be produced by digesting an appropriate substrate "blank" and two spiked samples of the same substrate spiked with the same standards and at the same levels of the LCS.

6.6 QUALITY CONTROL TRACKING AND DATA REVIEW

The QC data is considered acceptable and actual samples results can be evaluated and reported by the analyst if all QC samples are within established control limits.

6.7 CORRECTIVE ACTION

If a quality control measure fails, corrective action is taken and documented to ensure the accuracy of the data that is reported. Examples of when corrective action sheets are filled out are:

- A sample or QC is re-analyzed. This may be due to the QC parameter failing or mislabeling of samples.
- Samples are reported with a QC result (blank, spike matrix) parameter out of control. In this case, not only should a corrective action be initiated, but the data must be flagged.
- A deviation from the normal SOP for the method is discovered (*e.g.* a digestion goes down to dryness or a different concentration of reagent is used) and the sample is analyzed and reported.
- An error in a previously reported sample is discovered

7.0 SAMPLE MANAGEMENT

7.1 The procedures for sample management are detailed in the Great Lakes Analytical SOP for sample receipt into the laboratory.

7.2 Sample Schedule: Analysts keep track of sample throughput by using the Laboratory Information Management System (LIMS). The system is checked daily and a hard copy generated. Samples for this method are queued under "METP" The information includes:

- Client name.
- Sample numbers.
- Project name.
- Matrix.
- Hold time and turnaround time.

8.0 METHOD VALIDATION

8.1 QUALITY CONTROL BOOK

Method validation must be performed before any actual samples can be analyzed. Method validation studies are required to be stored in the QC logbook Method exception studies must also be performed to validate any exception taken by proving equivalency with the unaltered method The contents of the QC book include:

- Copy of the GLA Quality Assurance Program
- Copies of GLA SOP and source methods.
- Copy of the precision and accuracy study for the method
- Copies of all method detection limit studies and dates in use.
- Check standard recovery tabulations and control limits.
- Spike and spike duplicate recovery tabulations and control limits.
- Corrective action sheets.

8.2 QUALITY ASSURANCE PROGRAM

Internal audits will be performed periodically to assess analytical system performance Performance evaluation samples will be analyzed periodically to assess laboratory performance (Refer to the GLA Quality Assurance Program)

8.3 METHOD DETECTION LIMIT STUDY

8.3.1 The method detection limit (MDL) is defined as the minimum concentration of analyte that can be determined with 99% confidence. It is determined as follows:

- Prepare a minimum of seven replicate samples at a concentration at or near the expected MDL. Carry these replicates through the entire sample preparation procedure and analysis.
- Calculate the MDL by taking the standard deviation of the results of the seven replicates and multiply by the Student's t value at n-1 degrees of freedom (3.143 for seven replicates).

8.3.2 Other factors such as matrix effects and instrument noise may affect the attainable detection limit. These should be quantified if possible and taken in to account when determining an MDL as the obtainable detection level may be artificially elevated due to these factors.

8.3.3 A new MDL study must be performed to re-evaluate the method if any major instrument maintenance or service is performed, if any new method exceptions or changes are made or at least annually.

9.0 EQUIPMENT

9.1 Beakers. Griffin type, 250-mL size.
9.2 Watch covers, ribbed 90-mm diameter.
9.3 Volumetric flasks, 25-100 mL (wide mouth).
9.4 Glass funnels.
9.5 Filter paper - 9 and 15 cm. Whatman 41, or equivalent.
9.6 Sample containers, 50 or 100-mL capacity, metal-free.
9.7 Hotplate, adjustable, capable of maintaining a constant temperature for samples of 90-95°C. Monitor temperature of the hotplate by placing an Erlenmeyer flask with approximately 100 mL of cooking oil at the center of the hotplate, and reading the temperature with an ASTM thermometer positioned with the bulb against the bottom of the flask. The temperature must be at least 140°C. Record temperatures in the log book.
9.8 Analytical balance, calibrated - capable of weighing to nearest 0.1 g for soil/sediment/sludge samples 0.001 g for paints
9.9 Hot block digestion apparatus:
- HotBlock, Environmental Systems, set to maintain a sample temperature of 90-95°C
- Polyolefin digestion vessels, 50-mL size, with watch covers and snap-on caps.

10.0 STANDARDS AND REAGENTS

10.1 Reagent water - ASTM Type II Water (DI water).
10.2 Nitric acid - concentrated HNO_3, ACS/reagent grade, Fisher no. A509. **CAUTION:** Nitric acid is corrosive.
10.3 Hydrochloric acid - concentrated HCl, ACS/analytical reagent grade, Fisher no. A508. **CAUTION:** Hydrochloric acid is corrosive.
10.4 Hydrogen peroxide - 30% H_2O_2, ACS/analytical reagent grade Fisher no. H325. **CAUTION:** Hydrogen peroxide is an oxidizer
10.5 Spiking standards - GLA-SPK-1A and -4B, Inorganic Ventures. GLA-SPK-EM (earth metals spike) prepared from individual 10,000 ppm solutions (from Inorganic Ventures) for final concentrations of 2000 ppm of Na, K, Ca, and Mg (Refer to Appendix B for concentrations and volumes spiked.)

11.0 PROCEDURE

NOTE: Method validation (section 8.0) must be performed before samples can be analyzed.

11.1 SELECTION OF DIGESTION PROCEDURE

The appropriate method for the required metal analysis must be referenced in order to select the proper digestion procedure. There are several methods for digestions which can be selected based upon the matrix type of the sample and the type of digestion being performed. Use Table 1 to determine which method is most applicable to the samples being analyzed. The proper digestion procedure is selected from Table 2.

Table 1.
Digestion Method Reference Chart.

Analysis	Method Reference	Microwave Digestions	Standard Digestions		
			ICP/FLAA	GFAA	Special
Total Metals	SW-846	3051A	3050B + HCl	3050B + HNO_3	7060A (As) 7740A (Se)
	EPA	n/a	200.7	200.9	206.2 (As) 270.2 (Se)
Air Filters	NIOSH	n/a	7082	7082	n/a

Table 2.
Procedure Selection Table.

Digestion Type	Analysis Type	Analysis Method	Applicable Method(s)	Digestion Procedure
Standard	Total Metals	Any (1)	SW-846 3050B EPA 200.9 (3)	11.4 (GEN)
Standard	Air Filter - Lead Only	Any (1)	NIOSH 7082	11.4 (GEN)
Standard	Total Metals (2)	ICP/FLAA	SW-846 3050B EPA 200.7 (4)	11.5 (ICP)
HotBlock	Total Metals	Any (1)	SW-846 3050B	11.6 (HB)

(1) Any analytical method refers to GLA routine methods. ICP, GFAAS, and FLAA. These digests are not suitable for analysis of mercury or hexavalent chromium.
(2) For samples requiring addition of hydrochloric acid. This procedure produces digestates which can only be analyzed by ICP-OES.
(3) Samples are refluxed with nitric acid for metals determination by all analytical methods.
(4) Samples are refluxed with hydrochloric acid for metals determination by ICP-OES only.

11.2 Assemble all materials and equipment required for the procedure. A daily calibration check of the analytical balance must have been performed prior to its use in weighing samples or standard materials. Record all pertinent sample information in the log book(s) ***before beginning the analysis***.

CAUTION: All hotplate digestions must be performed in a fume hood

11.3 PREPARATION OF QUALITY CONTROL AND TEST SAMPLES

11.3.1 Soil, sediment, and other solid samples:

- Samples - A representative 2.0 g (1.0 g for hotblock digestion, section 11.6) aliquot is weighed into a clean beaker (or digestion tube for hotblock digestion).
- Matrix spikes - Measure two additional aliquots of one sample, with weights similar to the test sample weight, and making sure each aliquot is homogeneous and representative of the entire sample. Accurately aliquot 0.1 mL each of GLA-SPK-1A, -4B, and -EM into the sample replicates, and mark them as MS and MSD.

11.3.2 Sludge/high water content samples:

- Samples - Each sample should be well mixed before taking a representative portion for digestion. If the sample contains significant water, upon client request, a dry weight determination may be performed prior to digestion, and the sample size adjusted and/or calculated as follows:

$$\textit{sample weight (g)} = \frac{\textit{2.0 (1.0 for hotblock) g}}{\textit{dry weight (as decimal percent)}}$$

- Matrix spikes - Measure two additional aliquots of one sample, with weights similar to the test sample weight, and making sure each aliquot is homogeneous and representative of the entire sample. Accurately aliquot 0.1 mL each of GLA-SPK-1A, -4B, and -EM into the sample replicates. Add 5 mL of reagent water to each, washing the spike solutions into the beakers or vessels. Mark as MS and MSD.

11.3.3 Wipes samples (surrogate matrix QC):

- Samples - Transfer the entire wipe into a clean beaker along with any liquid and/or loose material which has fallen off the wipe. Rinse the sample container with three successive portions of reagent water, adding each rinsate to the beaker.
- Surrogate matrix blank - Place a 9- or 15-cm Whatman 41 filter paper into a clean beaker. Add 15 mL of reagent water.
- Surrogate matrix spike samples - Place 9- or 15-cm Whatman 41 filter paper into two clean and dry beakers. Weigh 0.02-0.04 g of NIST SRM1579a onto the filter paper. Allow any paint dust from the SRM addition to settle, and record an accurate weight in the log book to the nearest 0.0001 g. Carefully add 15 mL of reagent water

11.3.4 Paint/paint dust samples:

- Samples - Weigh as large a portion as possible, up to 2 g (accurately to the nearest 0.0001 g), into a clean beaker. Record the weight(s) in the log book.
- Surrogate matrix spike samples - Place 9 (or 15) cm Whatman 41 filter paper into two clean and dry beakers. Weigh 0.02-0.04 g of NIST SRM1579a onto the filter paper. Allow any paint dust from the SRM addition to settle, and record an accurate weight in the log book to the nearest 0.0001 g. Carefully add 15 mL of reagent water.

11.4 HOTPLATE DIGESTION OF SOLIDS FOR ANALYSIS BY ICP-OES, GFAAS, OR FLAA (GEN)

NOTE: Metal analytes for which this digestion is applicable include:
Al, As, Ba, Be, Cd, Ca, Cr (tot), Co, Cu, Fe, Pb, Mg, Mn, Mo, Ni, K, Na, Sb, Se, Tl, V, Zn

11.4.1 Add 5 mL of reagent water (except for wipes samples), 5 mL of concentrated HNO_3 and several boiling chips to each sample, cover with watchglasses and mix

11.4.2 Place on a hotplate and maintain at 90-95°C for 15 minutes. Remove and cool.

11.4.3 Add an additional 5 mL of concentrated HNO_3 to each sample, cover, and return to the hotplate for 30 minutes. Remove and cool.

11.4.4 Add a third 5 mL portion of concentrated HNO_3 to each sample, cover, and return to the hotplate for 30 minutes. Allow solutions to evaporate to approximately 5 mL. Remove and cool.

11.4.5 After the samples have cooled, add 2 mL of reagent water and 3 mL of 30% hydrogen peroxide to each. Warm gently if necessary to start the peroxide reaction. Heat until the effervescence subsides. Make further 1 mL additions of hydrogen peroxide until the effervescence is minimal, or the general sample appearance remains unchanged. Return to the hot plate for 15 minutes to destroy excess peroxide

11.4.6 Transfer the digestate to a 100-mL volumetric flask. Dilute to the mark with reagent water and mix. If samples are to be analyzed immediately, filter the digestate through a Whatman 41 filter paper into a metal-free container. Otherwise, samples may be allowed to settle 1 hour or overnight, prior to analysis. The container should be labeled with:

- GLA Sample I.D.
- Matrix type
- Date digested
- Dilution factor, if other than standard weight or volume (where applicable)

11.4.7 The samples are ready for analysis by ICP, GFAAS, or FLAA.

11.5 HOTPLATE DIGESTION OF SOLIDS FOR ANALYSIS BY ICP-OES OR FLAA ONLY (ICP)

NOTE: Metal analytes for which this digestion is applicable include:
Al, Ba, Be, Cd, Ca, Cr (tot), Co, Cu, Fe, Pb, Mg, Mn, Mo, Ni, K, Na, Tl, V, and Zn.

11.5.1 Add 5 mL of reagent water (except for wipes samples), 5 mL of concentrated HNO_3, and several boiling chips to each sample, cover with watch glasses, and mix.

11.5.2 Place on a hotplate and maintain at 90-95°C for 15 minutes. Remove and cool

11.5.3 Add an additional 5 mL of concentrated HNO_3 to each sample, cover, and return to the hotplate for 30 minutes. Remove and cool.

11.5.4 Add a third 5 mL portion of concentrated HNO_3 to each sample, cover, and return to the hotplate for 30 minutes. Allow solutions to evaporate to approximately 5 mL. Remove and cool.

11.5.5 After the samples have cooled, add 2 mL of reagent water and 3 mL of 30% hydrogen peroxide to each. Warm gently if necessary to start the peroxide reaction. Heat until the effervescence subsides. Make further 1 mL additions of hydrogen peroxide until the effervescence is minimal, or the general sample appearance remains unchanged. Return to the hot plate for 15 minutes to destroy excess peroxide.

11.5.6 Add 5 mL of concentrated HCl and 10 mL of reagent water to each sample. Cover and return to hotplate for 15 minutes. Remove and cool.

11.5.7 Transfer the digestate to a 100-mL volumetric flask. Dilute to the mark with reagent water and mix. Filter the digestate through a Whatman 41 filter paper into a metal-free container. The container should be labeled with:

- GLA Sample I.D.
- Matrix type
- Date digested
- Dilution factor, if other than standard weight or volume (where applicable)

11.5.8 The samples are ready for analysis by ICP or FLAA.

11.6 HOTBLOCK DIGESTION OF SOLIDS FOR ANALYSIS BY ICP-OES, GFAAS, OR FLAA (HB)

NOTE: Metal analytes for which this digestion is applicable include:
Al, As, Ba, Be, Cd, Ca, Cr (tot), Co, Cu, Fe, Pb, Mg, Mn, Mo, Ni, K, Na, Sb, Se, Tl, V, Zn.

NOTE: This procedure is not applicable for wipes samples.

11.6.1 Add 5 mL of reagent water (except for wipes samples) and 7.5 mL of concentrated HNO_3, to each sample. Cover and mix.

11.6.2 Place in digestor and heat for 75 minutes, maintaining sample temperatures of 95-100°C. Remove and cool.

11.6.3 After the samples have cooled slowly and carefully add 1 mL of 30% hydrogen peroxide to each. Allow vigorous reaction to subside. Place in digestor and heat for 15 minutes, maintaining sample temperatures of 95-100°C. Remove and cool.

11.6.4 Bring total sample volumes to 50 mL each with reagent water, cover and mix. Allow samples to settle at least 1 hour (or overnight). If immediate analysis is required, samples may be filtered through Whatman 41 filter paper. The container should be labeled with:

- GLA Sample I.D.
- Matrix type
- Date digested
- Dilution factor (where applicable)

11.6.5 The samples are ready for analysis by ICP, GFAAS, or FLAA.

12.0 MAINTENANCE AND TROUBLESHOOTING

12.1 GENERAL

Glassware should be cleaned appropriately to avoid sample contamination. Equipment should be kept clean and maintained to avoid sample contamination and assure proper operation. Manuals supplied by the manufacturers with the instrumentation typically have informational and troubleshooting sections.

12.2 TECHNICAL SUPPORT

Technical support is available from equipment manufacturers (for example, by telephone, fax, or e-mail). They can be a good resource when troubleshooting options have been exhausted. Technical support departments can readily supply part numbers.

13.0 REFERENCES

13.1 EPA Method 200.7: Inductively Coupled Plasma - Atomic Emission Spectrophotometric Method for Trace Element Analysis of Water and Wastes.

13.2 EPA Method 200.9: Determination of Trace Elements by Stabilized Temperature Graphite Furnace Atomic Absorption Spectrometry.

13.3 Method 3030: Preliminary Treatment of Samples, Sections E (Nitric Acid Digestion), F (Nitric Acid-Hydrochloric Acid Digestion), and K (Microwave-Assisted Digestion); Standard Methods for the Examination of Water and Wastewater, 18th Edition, 1992.
13.4 Method SW-846, 3050B: Acid Digestion of Sediments, Sludges, and Soils.
13.5 NIOSH Method 7082: Analysis of Lead in Air Filters.
13.6 Great Lakes Analytical Quality Assurance Program.
13.7 Great Lakes Analytical Chemical Hygiene Plan.
13.8 Great Lakes Analytical SOP for Login Department.
13.9 Great Lakes Analytical SOP for Hazardous Sample Management.

14.0 DEFINITIONS

See References

APPENDIX A.

METHOD EXCEPTIONS.

A.1 Section 1.0 - Sample Preservation

EPA 200 Series, section 4.1.4:

- Amounts of nitric and hydrochloric acids added to the preserved sample are in accordance with SW-846 Method 3005

SM-3030-F:

- Amounts of nitric and hydrochloric acids added to the preserved sample are in accordance with SW-846 Method 3005.

A.2 Section 11.4 - Sample Digestion (GEN)

EPA Method 200.7:

- Section 11.2.3 - Acid concentrations are made in accordance with SW-846, 3010B. The higher concentrations of acid will not compromise the digestion process.
- Sections 11.2.2-11.2.6 - Pre-concentration of samples is not performed unless detection levels are required that are below those attainable by current analytical procedures.

SM-3030-F:

- Additions of acid are made in accordance with SW-846, 3010B. The higher concentrations of acid will not compromise the digestion process.

A.3 Section 11.5 - Sample Digestion (ICP)

EPA Method 200.9:

- Section 11.3.3 - The addition of hydrochloric acid has been omitted an additional addition of nitric acid made its place. The interferences associated with chloride in the graphite furnace analysis are well documented in many reference documents (for example, EPA 200 Series, section 4.1.3).
- Sections 11.2.2-11.2.6 - Pre-concentration of samples is not performed unless detection levels are required that are below those attainable by current analytical procedures.

SM-3030-E

- Additions of acid are made in accordance with SW-846, 3010B. The higher concentrations of acid will not compromise the digestion process.

APPENDIX B.

STANDARD SPIKING LEVELS AND VOLUMES.

Standard	Aliquot/Volume	Aliquot/Volume	Aliquot/Volume	Aliquot/Volume	Aliquot/Volume
GLA-SPK-1A	0 10/100		0 05/50	0.10/50	0.10/50
GLA-SPK-3B		0.05/50		0.10/50	0.10/50
GLA-SPK-4B	0 10/100				
GLA-SPK-5			0.05/50	0.10/50	0.10/50
GLA-SPK-6					0.10/50
EARTH	0.10/100		0 05/50	0.05/50	

Set	Element	Soil	D H_2O FNC	D H_2O ICP	H_2O	TCLP/SPLP Ext.
R C R A	Ag	1.0	0.005		0.01	0.51
	As	0.03	0.015		0 03	0.03
	Ba	1.0		0.50	1.0	1 0
	Cd	1.0	0.001		0 002	0.502
	Cr	1.0	0 003	0.50	1.006	1.006
	Hg		0.001		0 002	0 002
	Pb	1 0	0.015		0.03	0.03
	Se	0.03	0.015		0.03	0.03
P R I R T Y	Be	1.0		0.50	1.0	1 0
	Cu	1.0	0.015	0.50	1.03	1 03
	Ni	1.0		0.50	1.0	1 0
	Sb	1.0	0.015	1 0	2.03	2.03
	Tl	2.0	0.015	1.0	2.03	2 03
	Zn	1.0		0.50	1.0	1.0
T A L	Al	1.0		0.5	1.0	1 0
	Co	1.0		0.5	1.0	1.0
	Fe	1.0		0.5	1.0	1.0
	Mn	1 0		0.5	1.0	1.0
	V	1.0		0.5	1.0	1.0
E A R T H	Ca	1.0		1.0	1.0	
	K	1.0		1.0	1.0	
	Li	1.0		1.0	1.0	
	Na	1.0		1 0	1.0	
	Mg	1.0		1 0	1.0	
E X T R A	B	1.0		1 0	2.0	2 0
	Mo	1.0		1 0	2.0	2 0
	Si	1.0		1 0	2.0	2.0
	Sn	1.0		1 0	2.0	2.0
	Ti	1.0		1 0	2.0	2 0

APPENDIX C.

METALS GLASSWARE PREPARATION

All glassware to be used in the preparation of solutions for metals analysis will be prepared according to the following procedure:

1. All beakers, funnels, flasks, stoppers and watch covers will be examined for gross contamination and soil removal.

2. Any analyst processing glassware through the laboratory dishwasher will use the appropriate detergent supplied.

3. All glassware shall subsequently be *hand-washed* using Neutrad soap (anionic detergent) and triple rinsed with tap water, then triple rinsed with de-ionized water, paying special attention to any glassware unduely etched, cracked or otherwise likely break and/or cause contamination of samples.

4. All glassware which will come into contact with samples to be analyzed for metals will be rinsed with a 50% Nitric Acid solution and triple rinsed with de-ionized water immediately prior to use. Glassware to be used for other inorganic analyses should be rinsed with an acid appropriate to the test. (e.g. - dilute sulfuric for nitrate/nitrite) and triple rinsed with de-ionized water.

Standard Operating Procedure for Analysis of Metals Using GFAA

GREAT LAKES ANALYTICAL

STANDARD OPERATING PROCEDURE

FOR

ANALYSIS OF METALS USING GFAA

GLA 7000 BG

Revision 2.0

Approved By:

Department Manager: _____ Date: 10/1/08

Quality Assurance Manager: _____ Date: 9/22/08

Laboratory Director: _____ Date: _____

1.0 APPLICABILITY

This standard procedure (SOP) provides instructions for the analysis of samples for trace metal content by graphite furnace atomic absorption (GFAA). The procedure for digestion of liquids is GLA 3015 BG, and for the digestion of solids is GLA 3050 BG. This SOP is an interpretation of EPA Method 200.9, Standard Methods no. 3113, Section B, and SW-846 no. 7000A. This SOP is to be used in conjunction with the analysts' in-laboratory training, the Great Lakes Analytical Chemical Hygiene Plan (CHP), and the Great Lakes Analytical Quality Assurance Program.

1.1 MATRICES

This method is applicable to digests prepared for GFAA analysis from GLA 3015 BG and GLA 3050 BG. Samples must be analyzed within 6 months (liquids preserved with nitric acid). Drinking water samples are analyzed per SM-3113-B.

1.2 REGULATORY APPICABILITY

40 CFR 121

2.0 SUMMARY

Aliquots of the digested samples are spiked with a matrix modifier and placed in the graphite tube via the instrument autosampler. First, a low current heats the tube to dry the sample. The second or charring stage, destroys organic matter and volatilizes other matrix components at an intermediate temperature. Finally, a high current heats the tube to incandescence and, in an inert atmosphere, atomizes the samples. The resultant ground-state atomic vapor absorbs radiation from the hollow cathode lamp, the absorption proportional to the analyte concentration. (See Appendix A for method exceptions.)

3.0 SAFETY

3.1 GENERAL

This SOP does not address all safety issues associated with its use. A reference file of material safety data sheets (MSDS's) is available to all personnel, along with the Great Lakes Analytical Chemical Hygiene Plan. Gloves are worn when handling chemicals and reagents.

3.2 CHEMICAL HYGIENE PLAN

The Great Lakes Analytical Chemical Hygiene Plan (CHP) is designed to establish safe work procedures and minimize exposure to hazardous chemicals encountered in the laboratory. The CHP provides information to employees regarding potential hazards and training to minimize these hazards.

3.3 HAZARDOUS SAMPLES

All samples that are received by the laboratory have the possibility of containing hazardous pollutants. They should be treated with caution at all times. Gloves are worn when handling samples. Also see the Great Lakes Analytical SOP for Hazardous Sample Management.

3.4 GRAPHITE FURNACE

The graphite furnace produces ultraviolet radiation. Do not view directly. The magnet of the furnace produces a field of about 8000 gauss RMS during the read stage. Keep pacemakers and magnetic storage media at a minimum distance of 30 cm (12 inches)

4.0 INTERFERENCES

4.1 All water samples must be preserved by the addition of nitric acid to a pH of 2 or less. A low bias could result due to metals adhering to the sides of the sample container or precipitating out of solution.

4.2 Elemental arsenic and selenium, as well as many of their compounds, are volatile. Samples are susceptible to analyte loss during digestion. Spiked samples are employed to determine whether proper digestion procedures were followed.

4.3 Non-specific absorption and light scattering can occur during analyses for arsenic and selenium during the atomization step. Zeeman background correction is used to minimize this effect.

4.4 Chlorides (>800 ppm) and sulfate (>200 ppm) interfere with the analysis of selenium. The addition of nickel nitrate as the matrix modifier decreases this interference

4.5 Sometimes an analyte is not completely volatilized and removed from the furnace. This can result in carryover which may be detected by analyses of blanks, and can be decreased by operating the furnace at full power at periodic intervals.

4.6 Chemical reaction of elements in the sample with graphite may occur at high temperatures. Elements that form carbides are barium, molybdenum, nickel, silicon, titanium, and vanadium. Using pryolytically coated tubes minimizes this problem

4.7 Daily monitoring test of the deionized water supply must have been performed and pass or meet appropriate criteria for analysis before the water can be used in sample preparation. All glassware to be used in the analysis must be cleaned and rinsed thoroughly with 50% nitric acid and DI water (see Appendix B). Periodic cleaning of sample preparation and analysis areas, will be performed

5.0 RECORD KEEPING

5.1 Each analyst is responsible for keeping accurate and up-to-date records of all analyses performed.

5.2 GFAA Log Book:

A log book will be maintained for all metals analyses performed on the GFAA. All information regarding samples processed in the lab will be entered into this book. This information will include but is not limited to.

- Sample matrix type
- GLA Sample I.D. (one complete for each set)
- LIMS batch reference number
- LCS and matrix spike information
- Analyst's signature and date analyzed

This log should also include any unique observations noted in regard to specific samples. Space will be reserved on each page for calculations and notes. All unused portions of logbook pages must be z'ed out.

5.3 An instrument log book is also kept for records of scheduled and unscheduled maintenance. All entries must be initialed and dated.

5.4 Sample Schedule - All samples will be tracked through the lab using GLA sample I.D. numbers generated by the GLA LIMS system.

6.0 QUALITY CONTROL

6.1 QUALITY CONTROL SAMPLES

Quality control samples are run at a minimum 5% frequency (*i.e.* one set with every batch of twenty or less samples). The results of these samples are used to gauge accuracy and precision of the method. These samples include method blanks (MB), lab control samples (LCS), matrix spikes (MS) and matrix spike duplicates (MSD). The quality control samples contain all reagents and are subjected to all preparation steps. They are processed and analyzed along with test samples. (See Appendix C for information on spike volumes and concentrations.)

6.2 METHOD BLANK

Matrix-matched method blanks (MB) containing all reagents and subjected to all preparation steps are processed and analyzed along with the samples. Method blanks must produce a concentration below the reporting limit (*e.g.* PQL, EQL, ...) for an analytical batch to be valid. These samples provide a measure of laboratory and/or reagent contamination. Test sample results are not corrected for the method blank concentrations.

6.3 LABORATORY CONTROL SAMPLE (LCS)

An external (independently sourced) reference standard is prepared within the working range of the method and analyzed with each matrix per batch of twenty or less samples (*i.e.* minimum 5% frequency). The results of the samples must be within established control limits, or where there is not enough data to calculate control limits, within **15%** of the known value.

6.4 MATRIX SPIKED SAMPLES

Matrix spiked samples (MS and MSD) will be analyzed with a minimum frequency of 5% (*e.g.* one set per 20 or less samples per matrix) and are used to determine accuracy and precision of a method. The matrix spiked samples will be spiked using the same standards used to spike the LCS samples. The analyzed result of the matrix spikes must be within established control limits, or where there is not enough data to calculate control limits, within 25% of the known value.

NOTE: For TCLP extracts, the sample matrix spike for As and Se (only) must be at least 50%. Other limits may be applicable per client request. If the recovery falls below this level, the method of standard additions must be used.

6.5 QUALITY CONTROL TRACKING AND DATA REVIEW

The QC data is considered acceptable and actual samples results can be evaluated and reported by the analyst if all QC samples are within established control limits.

6.6 CORRECTIVE ACTION

If a quality control measure fails, corrective action is taken and documented to ensure the accuracy of the data that is reported. Examples of when corrective action sheets are filled out are:

- A sample or QC is re-analyzed. This may be due to the QC parameter failing or mislabeling of samples.
- Samples are reported with a QC result (blank, spike matrix) parameter out of control. In this case, not only should a corrective action be initiated, but the data must be flagged.
- A deviation from the normal SOP for the method is discovered (*e.g.* a digestion goes down to dryness or a different concentration of reagent is used) and the sample is analyzed and reported.
- An error in a previously reported sample is discovered.

7.0 SAMPLE MANAGEMENT

7.1 The procedure for sample management are detailed in the Great Lakes Analytical SOP for sample receipt into the laboratory.

7.2 Sample Schedule: Analysts keep track of sample throughput by using the Laboratory Information Management System (LIMS). The system is checked daily and a hard copy generated. Samples for this method are queued under "METP". The information includes.

- Client name.
- Sample numbers.
- Project name.
- Matrix.
- Hold time and turnaround time.

8.0 METHOD VALIDATION

8.1 QUALITY CONTROL BOOK

Method validation must be performed before any actual samples can be analyzed. Method validation studies are required to be stored in the QC logbook. Method exception studies must also be performed to validate any exception taken by proving equivalency with the unaltered method. The contents of the QC book include:

- Copy of the GLA Quality Assurance Program.
- Copies of GLA SOP and source methods.
- Copy of the precision and accuracy study for the method
- Copies of all method detection limit studies and dates in use.
- Check standard recovery tabulations and control limits.
- Spike and spike duplicate recovery tabulations and control limits.
- Corrective action sheets.

8.2 QUALITY ASSURANCE PROGRAM

Internal audits will be performed periodically to assess analytical system performance. Performance evaluation samples will be analyzed periodically to assess laboratory performance. (Refer to the GLA Quality Assurance Program.)

8.3 ACCURACY AND PRECISION

Accuracy and precision for this method are tracked by analyzing spike and spike duplicate blanks (sample spikes and duplicates are also analyzed to check for matrix effects). The results are used to establish control limits - average ± 3 standard deviations for each analyte.

In addition, the GFAA instrument is calibrated at least daily, per each matrix analyzed, and the calibration checked using a Check Standard. The concentrations of the Check Standards must pass within limits indicated in Table 2 (within 10% of the expected values initially, and within 20% thereafter, after every 10 samples).

8.4 METHOD DETECTION LIMIT STUDY

8.4.1 The method detection limit (MDL) is defined as the minimum concentration of analyte that can be determined with 99% confidence. It is determined as follows:

- Prepare a minimum of seven replicate samples at a concentration at or near the expected MDL. Carry these replicates through the entire sample preparation procedure and analysis.
- Calculate the MDL by taking the standard deviation of the results of the seven replicates and multiply by the Student's t value at n-1 degrees of freedom (3.143 for seven replicates).

8.4.2 Other factors such as matrix effects and instrument noise may affect the attainable detection limit. These should be quantified if possible and taken in to account when determining an MDL as the obtainable detection level may be artificially elevated due to these factors.

8.4.3 A new MDL study must be performed to re-evaluate the method if any major instrument maintenance or service is performed, if any new method exceptions or changes are made or at least annually.

9.0 EQUIPMENT

9.1 Atomic Absorption Spectrophotometer, Varian SpectrAA-600Z, computer controlled, with Zeeman correction capacity, or equivalent.
9.2 Graphite tube atomizer - GTA 100Z, or equivalent.
9.3 Refrigerated water recirculator - set at 20-25°C. Coolflow CFT-33, or equivalent.
9.4 Four position lamp turrent.
9.5 Graphite tubes - pyrolytic coated partition tubes; except use L'vov platform tubes for cadmium analyses.
9.6 Autosampler programmable - PSD 97Z, 50 position, or equivalent.
9.7 Volumetric flasks, 25-100 mL.
9.8 Volumetric pipettors, adjustable volume.
9.9 Sample containers, minimum 100-mL capacity, metal-free.
9.10 Analytical balance, calibrated.

10.0 STANDARDS AND REAGENTS

10.1 Reagent water - ASTM Type II water (DI water).
10.2 Argon gas source at 41 psi
10.3 Nitric acid - concentrated HNO_3, ACS/reagent grade, Fisher no. A509 **CAUTION:** Nitric acid is corrosive
10.4 Hydrochloric acid - concentrated HCl ACS/analytical reagent grade, Fisher no. A508. **CAUTION:** Hydrochloric acid is corrosive
10.5 Sulfuric acid - concentrated H_2SO_4, ACS/analytical reagent grade, Fisher no. A300. **CAUTION:** Sulfuric acid is corrosive
10.6 Calibration standards - 1000 ppm, for individual analytes, from Spex CertiPrep Assurance, Inorganic Ventures, or Ultra Scientific. Prepare stock standard containing 3-6 ppm of analytes of interest, then working standards of 6-60 ppb (see Table 1).

10.7 Check standard - 30 ppb, for mid-range concentration. Preparation similarly to standard 10.5.
10.8 2% Palladium in nitric acid solution - VHG Labs no. xxx.
10.9 1% Nickel in nitric acid solution - VHG Labs no. xxx.
10.10 Citric acid - reagent grade, xxx no. xxx.
10.11 Ammonium phosphate, dibasic - $(NH_4)_2HPO_4$, Fisher no. xxx.
10.13 Matrix modifiers - for general analytes, use palladium/nickel/citric acid solution. Use appropriate modifiers when necessary for cadmium and silver.
Mixed modifier solution for As, Se, Pb: Aliquot 20 mL of 2% palladium solution, 10 mL of 1% nickel solution, 0.50 g of citric acid and dilute to 100 mL with reagent water.
Phosphate modifier for Cd: Dissolve 1 g of $(NH_4)_2HPO_4$ in 100 mL of reagent water.
Palladium modifier for Ag: Dilute 20 mL of 2% palladium solution to 100 mL with reagent water.

Table 1.
Digestion Methods and Standard Preparations.

MATRIX	DIGESTION METHOD	STANDARD PREPARED IN
Water Waste water Ground Water ASTM Leachate	3015	10% nitric acid in reagent water
Soil Sludge Solid Wipes Sludge waste Non-aqueous liquids	3050B 3010M	15% nitric acid in reagent water
TCLP Fluid 1	3015	10% nitric acid in TCLP Fluid 1
TCLP Fluid 2	3015	10% nitric acid in TCLP Fluid 2
SPLP Fluid 1	3015	10% nitric acid in SPLP Fluid 1
SPLP Fluid 2	3015	10% nitric acid in SPLP Fluid 2
Air filters	NIOSH 7082	15% nitric acid in reagent water

11.0 PROCEDURE

NOTE: Method validation (section 8.0) must be performed before samples can be analyzed.

NOTE: Metal analytes for which this method is applicable include: Sb, As, Ba, Cd, Cr, Cu, Pb, Se, Ag, and Tl. (See Appendix D for example wavelengths, detection levels, and concentration ranges.)

11.1 Assemble all materials and equipment required for the procedure. A daily calibration check of the analytical balance must have been performed prior to its use in weighing samples or standard materials. Record all pertinent sample information in the log book(s) ***before beginning the analysis***. The user's manual for the instrument can be consulted for more details on operation of the instrument.

11.2 INSTRUMENT CALIBRATION

11.2.1 The GFAA is calibrated daily before samples are analyzed in accordance with the instrument manufacturer's instructions. The standard curve includes one blank and a minimum of three standards, the lowest at or near the method detection limit. The calibration must pass with correlation coefficients, r^2, of at least 0.9950. The instrument performs two attempts to pass calibration before automatically pausing the run.

11.2.2 The calibration is checked using a Check Standard intially and after every 10 samples. The recovery of the analytes in the Check Standard must be within 10% of expected values initially, and within 20% thereafter.

11.3 ANALYSIS OF SAMPLES

11.3.1 A sequence of QC and test samples is prepared and analyzed:

1 Calibration blank
2 Check standard
3 Check standard
4 High standard
5 Calibration blank
6 10 Samples
7 Check standard
8 Calibration blank
9 10 Samples

Table 2: **Acceptance Criteria for Check Samples**

Calibration blank	< reporting limit
Check standard	±10%, unless second check standard passes
Check standard	±10%, unless first check standard passes
High standard	+10%
Calibration blank	< reporting limit
Continuing check - CCV	±20%
- CCB	< reporting limit

If any parameter fails, the problem must be corrected and tests passed before continuing with samples including possibly recalibrating the instrument.

11.3.2 A standard is run periodically to gauge the lifetime and performance of the graphite tubes. A lack of reproducibility, or a change in the signal for the standard, indicates that tube replacement is due. The ordinary life of a pyrolytic coated graphite tube is approximately 100-350 firings, depending upon the sample matrix and analyte.

11.3.3 If the concentration of a sample is greater than the highest standard plus 10%, the sample must be diluted and re-analyzed. The instrument automatically dilutes samples 1:4 and 1:24. If results are still out of range, manual dilutions must be performed.

11.3.4 Background correction (Zeeman) must be incorporated at all times. Background correction is important during flameless atomization, especially at wavelengths below 350 nm, and particularly for the analysis of arsenic and selenium in the presence of iron. False positive results may occur from the absorption or scattering of light from the lamp. This can be caused by the presence of gaseous molecular species, salt particles, or smoke in the sample beam.

11.4 CALCULATIONS

11.4.1 All analyte concentrations are multiplied by the dilution factor to obtain concentrations for the original samples.

11.4.2 For liquids digested using the microwave method, multiply concentrations by the factor 50/45 (= 1.11) to account for dilution of 45 mL of sample with 5 mL of nitric acid.

11.4.3 For solids, multiply concentrations by the factor 100/2 (= 50) to convert from mg/L to mg/kg of sample (from 2 g digested to 100 mL solution, or 1 g to 50 mL for HotBlock digestions). If the sample weight differs substantially from 2 g (or 1 g), use the factor 100/weight (or 50/weight) instead.

12.0 MAINTENANCE AND TROUBLESHOOTING

12.1 GENERAL

Glassware should be cleaned appropriately to avoid sample contamination. (See Appendix B.) Equipment should be kept clean and maintained to avoid sample contamination and assure proper operation. Manuals supplied by the manufacturers with the instrumentation typically have informational and troubleshooting sections.

12.2 TECHNICAL SUPPORT

Technical support is available from equipment manufacturers (for example by telephone, fax, or e-mail). They can be a good resource when troubleshooting options have been exhausted. Technical support departments can readily supply part numbers.

12.3 GRAPHITE FURNACE

The graphite shield (shroud) and chimney should be cleaned each time the graphite tube is replaced, using methanol.

The quartz windows should be regularly inspected. To clean, gently remove the windows, wash with 30% methanol, and dry with a Kimwipe. Never use coarse cloths or abrasive cleaning solutions.

The autosampler capillary and syringe should be inspected periodically for wear and damage. Repair or replace when required. Similarly, inspect and replace the electrodes when necessary (for example, when the absorbance peak for a standard begins to shift).

13.0 REFERENCES

13.1 EPA Method 200.9. Determination of Trace Elements by Stabilized Temperature Graphite Furnace Atomic Absorption Spectrometry.
13.2 Method 3113: Metals by Electrothermal Atomic Absorption Spectrometry, Section B (Electrothermal Atomic Absorption Spectrometric Method): Standard Methods for the Examination of Water and Wastewater, 18th Edition, 1992.
13.3 Method SW-846, 7000 Atomic Absorption Methods.
13.4 Great Lakes Analytical Quality Assurance Program.
13.5 Great Lakes Analytical Chemical Hygiene Plan.
13.6 Great Lakes Analytical SOP for Login Department.
13.7 Great Lakes Analytical SOP for Hazardous Sample Management.

14.0 DEFINITIONS

See References.

APPENDIX A.

METHOD EXCEPTIONS.

A.1 EPA Method 200.9:

- Section 11.3.3 -The addition of hydrochloric acid in step 11.3.3 has been omitted, and an additional additions of nitric acid are made in its place. The interferences associated with chloride in graphite furnace analysis are well documented (for example, in EPA 200 Series, section 4.1.3)
- Sections 11.2.2-11.2.6 - Pre-concentration of samples is not performed unless detection levels are required that are below those attainable by current analytical procedures

A.2 SM-3030-E:

Additions of acid are made in accordance with SW-846 3010B. The higher concentrations of acid will not compromise the digestion process.

A.3 SW-846 Methods 7060A and 7740A:

The digestates are not pre-mixed with nickel nitrate modifier. The modifier is added to the sampler by the instrument autosampler at the time of analysis.

A.4 EPA 200 Series, Methods 206.2 and 270.2:

The digestates are not pre-mixed with nickel nitrate modifier. The modifier is added to the sampler by the instrument autosampler at the time of analysis

APPENDIX B.

GLASSWARE PREPARATION FOR METAL ANALYSES.

All glassware to be used in the preparation of solutions for metals analysis will be prepared according to the following procedure:

B.1 All beakers funnels, flasks, stoppers and watch covers will be examined for gross contamination and soil removal.

B 2 Any analyst processing glassware through the laboratory dishwasher will use the appropriate detergent supplied.

B 3 All glassware shall subsequently be hand-washed using Neutrad soap (anionic detergent) and triple rinsed with tap water, then triple rinsed with de-ionized water, paying special attention to any glassware unduely etched, cracked or otherwise likely break and/or cause contamination of samples.

B.4 All glassware which will come into contact with samples to be analyzed for metals will be rinsed with a 50% Nitric Acid solution and triple rinsed with de-ionized water immediately prior to use. Glassware to be used for other inorganic analyses should be rinsed with an acid appropriate to the test. (e.g. - dilute sulfuric for nitrate/nitrite) and triple rinsed with de-ionized water.

APPENDIX C.

STANDARD SPIKING LEVELS AND VOLUMES.

Standard	Aliquot/Volume	Aliquot/Volume	Aliquot/Volume	Aliquot/Volume	Aliquot/Volume
GLA-SPK-1A	0 10/100		0.05/50	0.10/50	0.10/50
GLA-SPK-3B		0.05/50		0 10/50	0.10/50
GLA-SPK-4B	0.10/100				
GLA-SPK-5			0.05/50	0 10/50	0.10/50
GLA-SPK-6					0.10/50
EARTH	0 10/100		0.05/50	0.05/50	

Set	Element	Soil	D H_2O FNC	D H_2O ICP	H_2O	TCLP/SPLP Ext.
R C R A	Ag	1.0	0.005		0 01	0.51
	As	0.03	0.015		0 03	0.03
	Ba	1.0		0.50	1 0	1 0
	Cd	1.0	0.001		0.002	0.502
	Cr	1.0	0.003	0 50	1.006	1 006
	Hg		0.001		0.001	0 001
	Pb	1.0	0.015		0.03	0 03
	Se	0.03	0.015		0 03	0.03
P R I R T Y	Be	1.0		0.50	1.0	1.0
	Cu	1.0	0.015	0.50	1.03	1.03
	Ni	1.0		0 50	1 0	1.0
	Sb	1.0	0.015	1.0	2.03	2 03
	Tl	2.0	0 015	1 0	2 03	2 03
	Zn	1.0		0.50	1.0	1 0
T A L	Al	1.0		0.5	1.0	1.0
	Co	1.0		0.5	1.0	1 0
	Fe	1 0		0.5	1.0	1.0
	Mn	1.0		0 5	1.0	1.0
	V	1.0		0.5	1.0	1 0
E A R T H	Ca	1.0		1.0	1 0	
	K	1.0		1 0	1.0	
	Li	1.0		1 0	1.0	
	Na	1.0		1 0	1 0	
	Mg	1.0		1.0	1.0	
E X T R A	B	1 0		1 0	2.0	2.0
	Mo	1.0		1 0	2 0	2 0
	S	1.0		1 0	2.0	2 0
	Sr	1.0		1.0	2 0	2 0
	Ti	1.0		1 0	2 0	2 0

APPENDIX D.

EXAMPLE WAVELENGTHS, DETECTION LEVELS, AND CONCENTRATION RANGES FOR GFAA.

Element	Wavelength (nm)	IDL (µg/L)	Conc Range (µg/L)
Aluminum (Al)	309.3	3	20-200
Antimony (Sb)	217.6	3	20-300
Arsenic (As)	193.7	1	5-100
Barium (Ba)	553.6	2	10-200
Beryllium (Be)	234.9	0.2	1-30
Cadmium (Cd)	228.8	2	0.5-10
Chromium (Cr)	357.9	1	5-100
Cobalt (Co)	240.7	1	5-100
Copper (Cu)	324.7	1	5-100
Iron (Fe)	248.3	1	5-100
Lead (Pb)†	283.3	1	5-100
Manganese (Mn)	279.5	0.2	1-30
Molybdenum (Mo)	313.3	1	3-60
Nickel (Ni)	232.0	1	5-100
Selenium (Se)	196.0	2	5-100
Silver (Ag)	328.1	0.2	1-25
Tin (Sn)	224.6	5	20-300

† The more sensitive 217.0 nm wavelength is recommended for instruments with background correction capabilities.

Standard Operating Procedure for Analysis of Metals Using ICP

GREAT LAKES ANALYTICAL

STANDARD OPERATING PROCEDURE

FOR

ANALYSIS OF METALS USING ICP

GLA 6010 BG

Revision 2.0

Approved By:

Department Manager _____ Date 10/27/98

Quality Assurance Manager _____ Date _____

Laboratory Director: _____ Date: _____

1.0 APPLICABILITY

This standard procedure (SOP) provides instructions for analsis of samples for trace metal content by ICP-OES. The procedure for the digestion of liquids is GLA 3015 BG, and for the digestion of solids GLA 3050 BG. This SOP is an interpretation of EPA Methods 200.7, Standard Methods no. 3020, and SW-846 no. 6010B. This SOP is to be used in conjunction with the analysts' in-laboratory training, the Great Lakes Analytical Chemical Hygiene Plan (CHP), and the Great Lakes Analytical Quality Assurance Program.

1.1 MATRICES

This method is applicable to digests prepared for ICP analysis from GLA 3015 BG and GLA 3050 BG. Samples are to be analyzed for metals within 6 months. Drinking water samples are analyzed per SM-3113-B.

1.2 REGULATORY APPICABILITY

40 CFR 121

2.0 SUMMARY

This method describes a technique for the simultaneous (or sequential) multi-element determination of trace elements in solution. The basis of the method is the measurement of atomic emission by an optical spectroscopic technique. Samples are nebulized and the aerosol that is produced is transported to the ICP plasma torch where excitation occurs. The plasma torch consists of a flowing stream of argon which is ionized by an applied radio frequency of about 1.1 KW power (0.95-1.15 KW at 27-41 MHz). The field is inductively coupled to the ionized gas by a water cooled coil. Characteristic atomic-line emission spectra are produced by the high temperatures of the plasma torch (6000-8000 K). The spectra are dispersed by a grating spectrophotometer and the intensities of the lines are monitored by photomultiplier tubes. The currents from the photomultiplier tubes are controlled and processed by a computer system. A background correction technique is required to compensate for variable background contributions to the determination of trace elements.

3.0 SAFETY

3.1 GENERAL

This SOP does not address all safety issues associated with its use. A reference file of material safety data sheets (MSDS's) is available to all personnel, along with the Great Lakes Analytical Chemical Hygiene Plan. Gloves are worn when handling chemicals and reagents.

3.2 CHEMICAL HYGIENE PLAN

The Great Lakes Analytical Chemical Hygiene Plan (CHP) is designed to establish safe work procedures and minimize exposure to hazardous chemicals encountered in the laboratory. The CHP provides information to employees regarding potential hazards and training to minimize these hazards.

3.3 HAZARDOUS SAMPLES

All samples that are received by the laboratory have the possibility of containing hazardous pollutants. They should be treated with caution at all times. Gloves are worn when handling samples. Also see the Great Lakes Analytical SOP for Hazardous Sample Management.

3.4 PLASMA TORCH

The ICP plasma torch produces temperatures of 6000-8000 K and high levels of ultraviolet radiation. All instrument safety interlocks and shields must be in place and operational at all times.

4.0 INTERFERENCES

4.1 All water samples must be preserved by the addition of nitric acid to a pH of 2 or less. A low bias could result due to metals adhering to the sides of the sample container or precipitating out of solution

4.2 Spectral interferences can be caused by the overlap of a spectral line from another element, unresolved overlap of molecular band spectra, background contribution, or stray light from the line emission of high-concentration elements. Spectral overlap can be corrected after monitoring the interfering element. Each metal must be optimized and the best wavelength chosen. Unresolved overlap requires selection of another wavelength. Background contribution and stray light can be compensated for by performing background correction. An Interference Check Standard and Blank are analyzed at the beginning and end of each day's analyses, and/or every 8 hours, to evaluate the performance of the instrument.

4.3 Changes in viscosity and surface tension can cause significant inaccuracies by interfering with sample flow to the plasma torch, especially in samples containing large amounts of dissolved solids. Physical interferences can be reduced by diluting the sample, by internal standardization with yttrium, or by using standard additions method.

For internal standarization, yttrium is added at a concentration of 1 ppm to all standards, blanks, and samples by the instrument. Sample intensities are adjusted for changes in yttrium response as a function of the instrument program.

4.4 Chemical interferences are characterized by molecular compound formation, ionization effects, and solute vaporization effects. Normally, these effects are not substantial with the ICP technique. They can be minimized by careful selection of operating parameters, buffering of samples, matrix matching, and standard additions procedures. Lithium carbonate (200 ppm) is automatically mixed with all standards and samples before analysis for buffering.

4.5 Daily monitoring test of the deionized water supply must have been performed and pass or meet appropriate criteria for analysis before the water can be used in sample preparation. All glassware to be used in the analysis must be cleaned and rinsed thoroughly with DI water. Periodic cleaning of sample preparation and analysis areas, will be performed.

5.0 RECORD KEEPING

5.1 Each analyst is responsible for keeping accurate and up-to-date records of all analyses performed.

5.2 ICP Log Book

A log book will be maintained for all metals analyses performed on the ICP. All information regarding samples processed in the lab will be entered into this book. This information will include but is not limited to:

- Method reference number
- Sample matrix type
- GLA Sample I.D. (one complete for each set)

- LIMS batch reference number
- LCS and matrix spike information
- Analyst's signature and date analyzed
- Reviewer's signature and date, where applicable
- All dilution factors

This log should also include any unique observations noted in regard to specific samples. Space will be reserved on each page for calculations and notes. All unused portions of logbook pages must be z'ed out.

5.3 An instrument log book is also kept for records of scheduled and unscheduled maintenance. All entries must be initialed and dated.

5.4 Sample Schedule - All samples will be tracked through the lab using GLA sample I.D. numbers generated by the GLA LIMS system.

6.0 QUALITY CONTROL

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Quality control samples are run at a minimum 5% frequency (*i.e.* one set with every batch of twenty or less samples). The results of these samples are used to gauge accuracy and precision of the method. These samples include method blanks (MB), lab control samples (LCS), matrix spikes (MS) and matrix spike duplicates (MSD). The quality control samples contain all reagents and are subjected to all preparation steps. They are processed and analyzed along with test samples.

6.2 METHOD BLANK

Matrix-matched method blanks (MB) containing all reagents and subjected to all preparation steps are processed and analyzed along with the samples. Method blanks must produce a concentration below the reporting limit (*e.g.* PQL, EQL, ...) for an analytical batch to be valid. These samples provide a measure of laboratory and/or reagent contamination. Test sample results are not corrected for the method blank concentrations.

6.3 LABORATORY CONTROL SAMPLE (LCS)

An external (independently sourced) reference standard is prepared within the working range of the method and analyzed with each matrix per batch of twenty or less samples (*i.e.* minimum 5% frequency). The results of the samples must be within established control limits, or where there is not enough data to calculate control limits, within 15% of the known value. Appendix A contains information on spiking volumes and concentrations.

6.4 MATRIX SPIKED SAMPLES

Matrix spiked samples (MS and MSD) will be analyzed with a minimum frequency of 5% (*e.g.* one set per 20 or less samples per matrix) and are used to determine accuracy and precision of a method. The matrix spiked samples will be spiked using the same standards used to spike the LCS samples. The analyzed result of the matrix spikes must be within established control limits, or where there is not enough data to calculate control limits, within 25% of the known value.

6.5 INTERFERENCE CHECKS

The ICP instrument is checked initially and following analytical runs for interferences using an Interference Check Standard and an Interference Check Blank. These are samples containing high concentrations of interfering metals (Al, Ca, Mg, Fe). The Interference Check Standard also contains spiked analytes of interest (Ba, Cd, Cr, Pb, Ag).

6.6 QUALITY CONTROL TRACKING AND DATA REVIEW

The QC data is considered acceptable and actual samples results can be evaluated and reported by the analyst if all QC samples are within established control limits.

6.7 CORRECTIVE ACTION

If a quality control measure fails, corrective action is taken and documented to ensure the accuracy of the data that is reported Examples of when corrective action sheets are filled out are:

- A sample or QC is re-analyzed. This may be due to the QC parameter failing or mislabeling of samples.
- Samples are reported with a QC result (blank, spike matrix) parameter out of control. In this case, not only should a corrective action be initiated, but the data must be flagged
- A deviation from the normal SOP for the method is discovered (*e g* a digestion goes down to dryness or a different concentration of reagent is used) and the sample is analyzed and reported
- An error in a previously reported sample is discovered

7.0 SAMPLE MANAGEMENT

7.1 The procedure for sample management are detailed in the Great Lakes Analytical SOP for sample receipt into the laboratory.

7.2 Sample Schedule: Analysts keep track of sample throughput by using the Laboratory Information Management System (LIMS). The system is checked daily and a hard copy generated. Samples for this method are queued under "METP". The information includes:

- Client name.
- Sample numbers.
- Project name.
- Matrix.
- Hold time and turnaround time.

8.0 METHOD VALIDATION

8.1 QUALITY CONTROL BOOK

Method validation must be performed before any actual samples can be analyzed. Method validation studies are required to be stored in the QC logbook. Method exception studies must also be performed to validate any exception taken by proving equivalency with the unaltered method. The contents of the QC book include:

- Copy of the GLA Quality Assurance Program.
- Copies of GLA SOP and source methods.
- Copy of the precision and accuracy study for the method
- Copies of all method detection limit studies and dates in use
- Check standard recovery tabulations and control limits.
- Spike and spike duplicate recovery tabulations and control limits.
- Corrective action sheets

8.2 QUALITY ASSURANCE PROGRAM

Internal audits will be performed periodically to assess analytical system performance Performance evaluation samples will be analyzed periodically to assess laboratory performance. (Refer to the GLA Quality Assurance Program)

8.3 ACCURACY AND PRECISION

Accuracy and precision for this method are tracked by analyzing spike and spike duplicate blanks (sample spikes and duplicates are also analyzed to check for matrix effects). The results are used to establish control limits - average ± 3 standard deviations for each analyte.

In addition, the ICP instrument is calibrated daily, and the calibration checked using a Check Standard. Each individual analyte calibration must have a correlation coefficient, r^2, of at least 0 9950 to be usable. The concentrations of the Check Standard must be within 10% of the expected values

8.4 METHOD DETECTION LIMIT STUDY

8.4.1 The method detection limit (MDL) is defined as the minimum concentration of analyte that can be determined with 99% confidence. It is determined as follows:

- Prepare a minimum of seven replicate samples at a concentration at or near the expected MDL. Carry these replicates through the entire sample preparation procedure and analysis.
- Calculate the MDL by taking the standard deviation of the results of the seven replicates and multiply by the Student's t value at n-1 degrees of freedom (3 143 for seven replicates).

8 4.2 Other factors such as matrix effects and instrument noise may affect the attainable detection limit. These should be quantified if possible and taken in to account when determining an MDL as the obtainable detection level may be artificially elevated due to these factors.

8.4.3 A new MDL study must be performed to re-evaluate the method if any major instrument maintenance or service is performed. if any new method exceptions or changes are made, or at least annually.

9.0 EQUIPMENT

9.1 ICP Emission Spectrophotometer, TJA 61E TRACE. Liberty 100 or equivalent
9.2 Volumetric flasks, 25-100 mL size.
9.3 Volumetric pipets, various sizes.

10.0 STANDARDS AND REAGENTS

10.1 Reagent water - ASTM Type II water (DI water). Type I reagent water should be used for the analysis of earth metals and low level lead.

10.2 Nitric acid - concentrated HNO_3, ACS/reagent grade. Fisher no. A509. **CAUTION:** Nitric acid is corrosive.

10.3 Hydrochloric acid - concentrated HCl, ACS/analytical reagent grade, Fisher no A508. **CAUTION:** Hydrochloric acid is corrosive.

10 4 Sulfuric acid - concentrated H_2SO_4 - ACS/analytical reagent grade, Fisher no. A300. **CAUTION:** Sulfuric acid is corrosive.

10 5 Calibration standards - Standards are prepared in 10% nitric acid Aliquot 1000 ppm individual analyte standards (purchased from Spex CertiPrep Assurance, Inorganic Ventures, or Ultra Scientific) for high standard (level 4) per Table 1 into a 100-mL volumetric flask. Add 10 mL of concentrated HNO_3, dilute to the mark with reagent water and mix Prepare the medium standard (level 3) by dilution of the level 4 standard, 10 mL of level 4, 10 mL of concentrated HNO_3, to 100 mL final volume. Prepare the low standard (level 2) by dilution of the level 3 standard, 10 mL of level 3, 10 mL of concentrated HNO_3, to 100 mL final volume. The calibration blank (level 1) is prepared by diluting 10 mL of concentrated HNO_3 to 100 mL final volume.

10.6 Spiking solutions - GLA-SPK-1A and -4B, purchased from Inorganic Ventures; GLA-SPK-EM (earth metals spike) prepared from individual 10,000 ppm solutions (from Inorganic Ventures) for final concentrations of 2000 ppm of Na, K, Ca, and Mg. As, Se, Zr standard - 1000 ppm.

10.7 Calibration check standard - Add 50 mL of concentrated nitric acid to a 500-mL volumetric flask. Accurately aliquot 1.0 mL each of GLA-SPK-1A, -4B, and -EM into the volumetric flask. Aliquot 1.0 mL each of secondary As, Se, Zr 1000 ppm standards into the flask. Dilute to the mark with reagent water and mix.

10.8 Interference check solution - 5000 ppm Al, Ca, Mn, and 2000 ppm Fe, Inorganic Ventures no. CLPP-ICS-A

10.8 Interference check standard ICS-A - Aliquot 50 mL of concentrated sulfuric acid and 50 mL of CLPP-ICS-A into a 500-mL volumetric flask. Dilute to the mark with reagent water and mix.

10.9 Interference check standard ICS-B - Aliquot 50 mL of concentrated sulfuric acid and 50 mL of CLPP-ICS-A into a 500-mL volumetric flask. Then, accurately aliquot 1.0 mL each of GLA-SPK-1A, -4B, and -EM into the volumetric flask. Aliquot 1.0 mL each of secondary As, Se, Zr 1000 ppm standards into the flask. Dilute to the mark with reagent water and mix.

10.10 Yttrium standard - 10,000 ppm, purchased from Spex CertiPrep Assurance, Inorganic Ventures, or Ultra Scientific.

10.11 Lithium carbonate - Li_2CO_3 powder, Fisher no. 5840 or Mallinckrodt no. L119.

10.12 Buffer/internal standard solution - Weigh approximately 10.7 g of Li_2CO_3 and place in a new, clean 2-L fluorinated plastic bottle. Add 1 L of reagent water. Then add 1.0 mL of 10,000 ppm yttrium standard. Carefully add 200 mL of concentrated HNO_3 (Solution will effervesce due to release of carbon dioxide.) Dilute to approximately 2 L with reagent water and mix.

10.13 Rinse solution - 10% nitric acid in reagent water.

11.0 PROCEDURE

NOTE: Method validation (section 8.0) must be performed before samples can be analyzed.

NOTE: See Table 1 for the analytes for which this method is applicable. See Appendix B for some recommended wave-lengths, estimated instrumental detection limits (IDL), and potential interferences (at the 100 mg/L level).

11.1 Assemble all materials and equipment required for the procedure. A daily calibration check of the analytical balance must have been performed prior to its use in weighing samples or standard materials. Record all pertinent sample information in the log book(s) ***before beginning the analysis***.

Table 1.
Preparation and Concentrations of Calibration Standard Solutions.

ELEMENT	Volume (mL) of 1000 ppm Standard to Prepare High Standard	High Standard (Level 4) Concentration (ppm)	Medium Standard (Level 3) Concentration (ppm)	Low Standard (Level 2) Concentration (ppm)
Ag	1.0	10.0	1.00	0.100
Al	2.5	25.0	2.50	0.250
As	0.5	5.0	0.50	0.050
B	1.0	10.0	1.00	0.100
Ba	2.5	25.0	2.50	0.250
Be	0.5	5.0	0.50	0.050
Ca	2.5	25.0	2.50	0.250
Cd	0.5	5.0	0.50	0.050
Co	1.0	10.0	1.00	0.100
Cr	1.0	10.0	1.00	0.100
Cu	1.0	10.0	1.00	0.100
Fe	2.5	25.0	2.50	0.250
K	2.5	25.0	2.50	0.250
Mg	2.5	25.0	2.50	0.250
Mn	1.0	10.0	1.00	0.100
Mo	1.0	10.0	1.00	0.100
Na	2.5	25.0	2.50	0.250
Ni	1.0	10.0	1.00	0.100
Pb	0.5	5.0	0.50	0.050
Sb	1.0	10.0	1.00	0.100
Se	0.5	5.0	0.50	0.050
Sn	1.0	10.0	1.00	0.100
Ti	1.0	10.0	1.00	0.100
Tl	1.0	10.0	1.00	0.100
V	1.0	10.0	1.00	0.100
Zn	2.5	25.0	2.50	0.250

Note: See Section 10.5 for complete instructions on calibration standard preparation

11.2 INTERFERENCE CHECK STANDARD AND BLANK

An Interference Check Standard, containing high amounts of interfering elements and known concentrations of elements of interest, is analyzed at the beginning and the end of each sequence of samples. The interfering elements are the following concentrations: Al, Ca, Mg - 500 ppm, Fe - 200 ppm. The elements of interest are each spiked at 2.0 ppm (exceptTl, which is 4.0 ppm). Recoveries must be within ± 20% of the expected concentrations.

An Interference Check Blank, containing high amounts of interfering elements, is analyzed at the beginning and end of each sequence of samples. This blank contains the same concentrations of interfering elements as the check standard. The Interference Blank is analyzed for Ba, Cd, Cr, Pb, and Ag. The concentrations detected for these elements must not be above the reporting limits.

Internal Standard - Yttrium is added at a concentration of approximately 1.0 ppm to all standards, blanks, and samples by the instrument. The intensity is tracked to ensure proper instrument operation.

11.3 INSTRUMENT CALIBRATION

The ICP is calibrated daily before samples are analyzed. The standard curve includes one blank and three standards (4 levels). The correlation coefficient, r^2, must be at least 0.9950 for each analyte to be run.

The calibration is checked using a Check Standard initially and after every 10 (or fewer) samples. The recovery of the analytes in the Check Standard must be with 10% of expected values. Replicate integrations of the Check Standard must have a %RSD of ≤5%. For A2LA required work, the High Level Standard (Level 4)is used as a check of the calibration, and must be within +/-5% of the actual value.

11.4 OPERATION OF THE INSTRUMENT

11.4.1 Power up the instrument and ignite plasma according to the manufacturer's instructions.
11.4.2 Allow instrument to warm up at least 30 minutes
11.4.3 Perform system profile in accordance with the manufacturer's instructions using an approximately 5 ppm As standard.
11.4.4 Go to analysis section and call up method **6010PM1**.
11.4.5 Calibrate instrument using calibration standards. Each analyte to be used must have a correlation coefficient of at least 0.9950.
11.4.6 Run performance and instrument check samples:

	Sample	Criteria
A.	ICV (check standard)	±10%
B.	ICB (calibration blank)	< reporting limit
C.	High standard	±10%
D.	ICS-B	±20%
E.	ICS-A	< reporting limit (except Al, Ca, Fe, Mg)

11.4.7 If all criteria pass run samples with a CCV and CCB every 10 (or less) samples. The high standard, ICS-B, and ICS-A need to be re-analyzed at the end of the run, or every 8 hours

11.5 CALCULATIONS

11.5.1 Results are corrected for any spectral interferences and backgrounds (by the instrument software).

11.5.2 All analyte concentrations are multiplied by the applicable dilution factor (DF) to obtain concentrations for the original samples.

For waters/liquids:

$$\text{concentration (mg/L)} = \frac{\text{instr. result} \times \text{final digestate volume (mL)} \times \text{DF}}{\text{initial sample volume (mL)}}$$

For soils/solids/sludges:

$$\text{concentration (mg/kg)} = \frac{\text{instr. result} \times \text{final digestate volume (mL)} \times \text{DF}}{\text{initial sample weight (g)}}$$

To report result in dry weight, divide concentration result by decimal percent solids (*e.g.* if %solids is 89%, divide by 0.89).

For paints:

$$\text{concentration (\%)} = \frac{\text{instr. result} \times \text{final digestate volume (mL)} \times \text{DF}}{\text{initial sample weight (g)} \times 10{,}000}$$

10,000 is the factor for converting mg/kg (ppm) to percent.

For wipes:

amount (mg per wipe) = instr. result × final digestate volume (mL) × DF

To report in mg per square foot, divide result by area (supplied by client).
To convert to µg, multiply result by 1000

12.0 MAINTENANCE AND TROUBLESHOOTING

12.1 GENERAL

Glassware should be cleaned appropriately to avoid sample contamination. Equipment should be kept clean and maintained to avoid sample contamination and assure proper operation. Manuals supplied by the manufacturers with the instrumentation typically have informational and troubleshooting sections.

12.2 TECHNICAL SUPPORT

Technical support is available from equipment manufacturers (for example, by telephone, fax, or e-mail). They can be a good resource when troubleshooting options have been exhausted. Technical support departments can readily supply part numbers

12.3 CLEANING THE PLASMA TORCH

The plasma torch must be cleaned weekly. This is accomplished by soaking the torch in a solution of 1 part concentrated HCl and 3 parts concentrated HNO_3 overnight. The height of the torch will need adjustment when the torch is replaced.

13.0 REFERENCES

13.1 EPA Method 200.7: Inductively Coupled Plasma - Atomic Emission Spectrophotometric Method for Trace Element Analysis of Water and Wastes.
13.2 Method 3120: Metals by Plasma Emission Spectroscopy. Section B (Inductively Coupled Plasma Method): Standard Methods for the Examination of Water and Wastewater. 18th Edition, 1992.
13.3 Method SW-846, 3020B: Inductively Coupled Plasma - Atomic Emission Spectroscopy
13.4 Great Lakes Analytical Quality Assurance Program.
13.5 Great Lakes Analytical Chemical Hygiene Plan
13.6 Great Lakes Analytical SOP for Login Department.
13.7 Great Lakes Analytical SOP for Hazardous Sample Management.

14.0 DEFINITIONS

See References.

APPENDIX A.

STANDARD SPIKING LEVELS AND VOLUMES.

Standard	Aliquot/Volume	Aliquot/Volume	Aliquot/Volume	Aliquot/Volume	Aliquot/Volume
GLA-SPK-1A	0.10/100		0 05/50	0.10/50	0 10/50
GLA-SPK-3B		0.05/50		0.10/50	0 10/50
GLA-SPK-4B	0.10/100				
GLA-SPK-5			0.05/50	0.10/50	0.10/50
GLA-SPK-6					0.10/50
EARTH	0.10/100		0.05/50	0.05/50	

Set	Element	Soil	D H_2O FNC	D H_2O ICP	H_2O	TCLP/SPLP Ext.
R C R A	Ag	1.0	0.005		0.01	0.51
	As	0.03	0.015		0.03	0.03
	Ba	1.0		0 50	1.0	1.0
	Cd	1.0	0.001		0 002	0.502
	Cr	1.0	0.003	0.50	1.006	1.006
	Hg		0.001		0.001	0 001
	Pb	1.0	0.015		0 03	0.03
	Se	0 03	0.015		0.03	0.03
P R I R T Y	Be	1.0		0.50	1.0	1.0
	Cu	1.0	0.015	0.50	1.03	1.03
	Ni	1.0		0.50	1.0	1.0
	Sb	1.0	0.015	1.0	2.03	2.03
	Tl	2.0	0.015	1.0	2.03	2.03
	Zn	1.0		0.50	1.0	1.0
T A L	Al	1.0		0.5	1.0	1.0
	Co	1.0		0 5	1.0	1.0
	Fe	1.0		0 5	1.0	1.0
	Mn	1.0		0.5	1.0	1.0
	V	1.0		0.5	1.0	1.0
E A R T H	Ca	1.0		1.0	1.0	
	K	1.0		1.0	1.0	
	Li	1.0		1.0	1.0	
	Na	1.0		1 0	1 0	
	Mg	1.0		1.0	1.0	
E X T R A	B	1.0		1.0	2.0	2.0
	Mo	1 0		1 0	2 0	2 0
	Si	1.0		1.0	2.0	2.0
	Sn	1 0		1 0	2 0	2 0
	Ti	1 0		1 0	2 0	2 0

APPENDIX B.

EXAMPLE WAVELENGTHS, ESTIMATED INSTRUMENTAL DETECTION LIMITS (IDL), AND POTENTIAL INTERFERENCES AT THE 100 mg/L LEVEL.

Element	Wavelength (nm)	IDL (µg/L)	Interferent(s) *
Aluminum (Al)	308.215	30	Mn 0.2, V 1.4
Antimony (Sb)	206.833	21	Al 0.5, Cr 2.9, Fe 0.1, Ti 0.3, V 0.5
Arsenic (As)	193.696	35	Al 1.3, Cr 0.4, V 1.1
Barium (Ba)	455.403	0.9	
Beryllium (Be)	313.042	0.2	Ti 0.04, V 0.05
Boron (B)	249.678†	3.8	
Cadmium (Cd)	226.502	2.3	Fe 0.03, Ni 0.02
Calcium (Ca)	317.933	6.7	Cr 0.1, Mn 0.04, Ti 0.03, V 0.03
Chromium (Cr)	267.716	4.7	Mn 0.04, V 0.04
Cobalt (Co)	228.616	4.7	Cr 0.03, Fe 0.01, Ni 0.03, Ti 0.15
Copper (Cu)	324.754	3.6	Ti 0.05, V 0.02
Iron (Fe)	259.940	4.1	Mn 0.1
Lead (Pb)	220.353	28	Al 0.2
Lithium (Li)	670.784	2.8	
Magnesium (Mg)	279.079	20	Cr 0.1, Fe 0.1, Mn 0.3, Ti 0.1, V 0.1
Manganese (Mn)	257.610	0.9	Al 0.01, Cr 0.01
Mercury (Hg)	194.227†	17	
Molybdenum (Mo)	202.030	5.3	Al 0.05, Fe 0.03
Nickel (Ni)	231.604†	10	
Phosphorus (P)	213.618	51	
Potassium (K)	766.491	‡	
Selenium (Se)	196.026	50	Al 0.2, Fe 0.1
Silica (SiO_2)	251.611	17	
Silver (Ag)	328.068	4.7	
Sodium (Na)	588.995	19	Ti 0.08
Strontium (Sr)	407.771	0.3	
Thallium (Tl)	190.864	27	Al 0.3
Tin (Sn)	189.9890†	17	
Titanium (Ti)	334.941	5.0	
Vanadium (V)	292.402	5.0	Cr 0.05, Fe 0.01, Ti 0.02
Zinc (Zn)	213.856†	1.2	Cu 0.1, Ni 0.3

† second order.
‡ highly dependent on operating conditions and plasma position
* analyte concentration equivalents

Standard Operating Procedure for Organic Extraction and Sample Preparation for Semivolatile Determinative Methods

GREAT LAKES ANALYTICAL

STANDARD OPERATING PROCEDURE

FOR

ORGANIC EXTRACTION AND SAMPLE PREPARATION FOR

SEMIVOLATILE DETERMINATIVE METHODS

GLA 3500 BG

Revision 1.1

Approved By:

Department Manager: _____ Date: 10-27-98

Quality Assurance Manager: _____ Date: 10/27/98

Laboratory Director: _____ Date: _____

1.0 APPLICABILITY

This standard procedure (SOP) provides instructions for the selection and use of procedures for the extraction, dilution, and cleanup of samples for analysis by semivolatile determinative methods. This SOP is an interpretation of several EPA extraction methods, including 3500B, 3510C, 3550B, and 3580A, and cleanup methods 3620B, 3640A, 3660B, and 3665A. This SOP is to be used in conjunction with the analysts' in-laboratory training, the Great Lakes Analytical Chemical Hygiene Plan (CHP), and the Great Lakes Analytical Quality Assurance Program.

1.1 MATRICES

This SOP may be used for aqueous, soil/sediment, solid waste, and non-aqueous solvent-soluble waste samples.

1.2 REGULATORY APPLICABILITY

40 CFR 121

2.0 SUMMARY

2.1 Samples of known volume or weight are extracted with solvent, or diluted with solvent, in preparation for analysis. One of the following methods is used depending upon sample type:

- Aqueous samples are extracted using separatory funnel liquid-liquid extraction (method 3510C). For example, 1000 mL of sample is extracted using three 60 mL portions of methylene chloride (section 11.1).
- Soil/sediment samples are extracted using ultrasonic extraction (method 3550B). For example, 30 g of sample is extracted using three 100 mL portions of methylene chloride (sections 11.3 and 11.4).
- Samples for herbicide analysis are extracted and derivatized using diazomethane (method 8151, sections 11.2 and 11.5).
- Non-aqueous solvent soluble samples are diluted (method 3580A). For example, 1-2 g of sample is mixed with 10 mL of methylene chloride (section 11.6).

2.2 Some samples may be required to be placed through a cleanup procedure to eliminate interferences. Sample cleanup procedures are:

- Samples for PCB analysis are treated with sulfuric acid (method 3665A) to remove interferences (section 12.1). Sulfur cleanup is required following the sulfuric acid cleanup procedure.
- Soluble sulfur can be removed using copper (method 3660B, section 12.2).
- Florisil (magnesium silicate) may be used to separate analytes from interfering compounds (method 3620B, section 12.3).
- Cleanup using gel permeation chromatography (GPC, method 3640A) may be used to separate molecules of different sizes (section 12.4).

2.3 The resultant extracts are dried using anhydrous sodium sulfate and concentrated using Kuderna-Danish (K-D) apparatus, or in an automated concentration device. The extracts are analyzed, for example, per one of EPA methods 8015, 8081, 8082, 8151, 8270, or 8310.

3.0 SAFETY

3.1 GENERAL

This SOP does not address all safety issues associated with its use. A reference file of material safety data sheets (MSDS's) is available to all personnel, along with the Great Lakes Analytical Chemical Hygiene Plan

The toxicity or carcinogenicity of each reagent used in this SOP has not been precisely determined; however, each chemical should be treated as a potential health hazard. Exposure to these chemicals should be reduced to the lowest possible level. Gloves are worn when handling solvents (use nitrile gloves to avoid contamination with plasticizers).

3.2 CHEMICAL HYGIENE PLAN

The Great Lakes Analytical Chemical Hygiene Plan (CHP) is designed to establish safe work procedures and minimize exposure to hazardous chemicals encountered in the laboratory. The CHP provides information to employees regarding potential hazards and training to minimize these hazards.

3.3 HAZARDOUS SAMPLES

All samples that are received by the laboratory have the possibility of containing hazardous pollutants. They should be treated with caution at all times. Gloves are worn when handling samples (use nitrile gloves to avoid contamination with plasticizers) Also see the Great Lakes Analytical SOP for Hazardous Sample Management.

4.0 INTERFERENCES

4.1 Solvents, reagents, glassware, and other sample processing hardware may yield artifacts and/or interferences to sample analysis. All these materials are demonstrated to be free from interferences under the conditions of the analysis by analyzing method blanks. Soap residue (for example, sodium dodecyl sulfate), which causes a basic pH on glassware surfaces, may cause degradation of certain analytes. In general, glassware is washed using Contrad or Alconox detergent, and then rinsed thoroughly with organic-free deionized water, acetone, and finally with methylene chloride.

4.2 Phthalate esters contaminate many types of products found in the laboratory. Plastics, in particular, are not used because phthalates are commonly used as plasticizers and are easily extracted from plastic materials. Serious phthalate contamination may result at any time if consistent quality control is not practiced. Nitrile gloves must be used.

4.3 Materials causing interferences may be coextracted from a sample. If analysis of an extracted sample is prevented due to interferences, further cleanup of the sample extract may be necessary

5.0 RECORD KEEPING

5.1 Extraction logbooks contain records of analytical batches.

5.2 Analytical batch records must contain the following information:

5.2.1 Sample volume or weight.
5.2.2 Client name or sample number.
5.2.3 Great Lakes sample number.
5.2.4 Extraction method.
5.2.5 Analytical method.
5.2.6 Date(s) extracted and concentrated.
5.2.7 Lab batch ID number.
5.2.8 Extraction or dilution solvent, and lot number.
5.2.9 Final solvent (if different), and lot number.
5.2.10 Initials of analyst(s)
5.2.11 Lab lot ID# of spiking solution(s).
5.2.12 Final volume of extract.
5.2.13 Any "cleanup" methods used.

An example of a logbook page for an analytical batch record is attached to this SOP (see Attachment 1).

5.3 All unused portions of logbook pages must be z'ed out.

6.0 QUALITY CONTROL

6.1 For quality control, each water extraction batch contains a method blank (MB), and a blank spike (BS), and a blank spike duplicate (BSD) An analytical batch contains no more than 20 samples. Deionized water is used for water method blanks and spikes.

6.2 Each soil extraction batch (not more than 20 samples) contains a method blank (MB), a lab control spike (LCS), a matrix spike (MS), and a matrix spike duplicate (MSD). Clean sand is used for soil method blanks (MB) and blank spikes (LCS). Soil samples selected randomly by the LIMS are used for matrix spikes and matrix spike duplicates The extractionists can override this if insufficient sample is available, or if chosen sample is extremely dirty.

6.3 Surrogate compounds are added to all samples, blanks, and spikes in an analytical batch.

6.4 Descriptions of the standards used for spiking and as surrogates are given in the individual analytical method SOPs For example, method 8151 (Herbicides) uses a spiking standard containing 0.1 to 1.3 mg/mL of herbicide compounds and a surrogate of 100 µg/mL dichorophenylacetic acid (DCAA or DCPA).

7.0 SAMPLE MANAGEMENT

7.1 The procedure for sample management are detailed in the Great Lakes Analytical SOP for sample receipt into the laboratory

7.2 LIMS extraction batching procedure.

7.2.1 At the LIMS main menu screen, select B (batching), new batch.
7.2.2 At the Queue prompt type in "EXTR" and press F8
7.2.3 Highlight the test wanted from the list of available methods and double-click.
7.2.4 Deselect any samples by clicking on the corresponding √ (check mark).
7.2.5 Click on "Build Batch", then "Add QC". Press "Save".

7.2.6 At name prompt, enter initials of extractionist.
7.2.7 When the batch list appears on screen, highlight "Please Select A Printer", press "List" and choose the "SVOC LIMS Printer".
7.2.8 Select "OK" at all prompts.

8.0 METHOD VALIDATION

Each new extractionist will perform a series of extractions to establish the ability to generate acceptable precision and accuracy. For each analytical method:

8.1 Four 1000 mL blank water samples (method validation for water analysis), or four 30 g blank sand samples (method validation for soil analysis), are extracted and concentrated, each spiked with 1.0 mL of the QC spiking solution (see method 3500B, Section 8.2.4).
8.2 The extracts will be analyzed and the average percent recovery and the standard deviation of the percent recoveries for each component of the spikes will be calculated.
8.3 Acceptance criteria are found in the appropriate determinative method.
8.4 Documentation of these analyses will be maintained in the employee's training file.

9.0 EQUIPMENT

NOTE: The exact equipment necessary will depend upon the sample matrix, extraction performed, analytical method, and any clean-up(s) required.

9.1 Graduated cylinders - 1000-mL, for measuring volume of aqueous samples.
9.2 Separatory funnels - 2-L and 125-mL, with PTFE stopcocks and caps.
9.3 pH indicator paper - range to cover pH 0 to 13.
9.4 Solvent dispensers, for 30 to 100 mL (two 50-mL dispenses may be used for 100 mL)
9.5 Squirt bottles for solvents.
9.6 Benchtop shaker, for separatory funnels.
9.7 Laboratory timer, clock, or wristwatch.
9.8 Erlenmeyer flasks - 500 and 125-mL, for collecting sample extracts.
9.9 Filter funnels - 75 mm, fluted bowl, short stem.
9.10 Filter paper - Whatman No. 41 (or equivalent) to fit filter funnels.
9.11 Boiling chips, PTFE (Teflon).
9.12 Spatula, stainless steel or PTFE.
9.13 Glass Pasteur pipets.
9.14 Kuderna-Danish (K-D) apparatus, each consisting of:

- Concentrator tube - 10 mL, graduated.
- Evaporator flask - 500 mL.
- Snyder column - three-ball macro.
- Clamps - for securing glassware at ground-glass joints

9.15 Water bath - heated, with concentric ring cover, temperature setting on "High" for approximately 95°C
9.16 Oven, capable of maintaining 400-500°C.
9.17 Syringes, glass - 2.5 mL, 1.0 mL, and 100 µL.
9.18 Syringe filters - 0.2 µm, 13 mm, Acrodisk, Fisher no. SJFGO13NS.
9.19 Nitrogen blowdown apparatus - Organomation N-EVAP or equivalent, connected to nitrogen gas source, temperature setting at about "5" for approximately 50°C bath temperature.
9.20 Balance - top-loading, capable of accurately weighing to the nearest 0.01 g.
9.21 Beaker - 250 mL, for sonicating samples.

9.22 Ultrasonic disrupter - with minimum power of 300 watts, equipped with dual ¾" horns, Heat Systems XL, or equivalent.
9.23 Sonabox - used to decrease cavitation sound from disrupter.
9.24 Ultrasonic water bath - Branson 8210, or equivalent.
9.25 Automatic evaporative concentrator - Zymark Turbo Vap II.
9.26 Concentrator tubes - Zymark, 200 mL, 1.0 mL tip.
9.27 Glass chromatography column, 20 mm diameter, approximately 30 cm length.
9.28 HPLC for GPC cleanup, consisting of:

- Solvent pump - capable of delivering 5 mL/min.
- Sample injector - with 0.5 mL sample loop.
- GPC Cleanup columns - Waters Envirogel, 19 × 150 mm and 19 × 300 mm.
- UV absorbance detector - with mercury lamp for 254 nm.
- Flow transfer valve - for eluent to waste or collect.
- Integrator or chart recorder.
- Solvent supply and waste containers

10.0 STANDARDS AND REAGENTS

NOTE: The exact standards and reagents necessary will depend upon the sample matrix, extraction performed, analytical method, and any clean-up(s) required.

10.1 Reagent water - organic-free deionized (DI water), Fisher no. W5.
10.2 Acetone - pesticide grade or equivalent, Fisher no. A929.
10.3 Acetonitrile - pesticide grade or equivalent, Fisher no. A21.
10.4 Diethyl ether - pesticide grade or equivalent, Fisher no. E197.
10.5 Methanol - pesticide grade or equivalent, Fisher no. A453.
10.6 Hexane - pesticide grade or equivalent, Fisher no. H303.
10.7 Methylene chloride ($MeCl_2$) - pesticide grade or equivalent, Fisher no. D151.
10.8 Acetone/methylene chloride solution (1:1 v/v) - Mix 500 mL of acetone with 500 mL of methylene chloride in a 1-L bottle.
10.9 6%, 15%, and 50% Diethyl ether in hexane solution (v/v) - Mix proportionate volumes of diethyl ether and hexane in a 1-L bottle. For example, 60 mL ether and 940 mL hexane for 6%, 150 and 850 for 15%, or 500 and 500 for 50% (v/v) solutions.
10.10 Sodium hydroxide - pellets, NF/FCC grade, Fisher no. S320. **CAUTION:** Sodium hydroxide is corrosive
10.11 Sodium hydroxide solution (10 N) - Dissolve 40 g of sodium hydroxide (NaOH) in water and dilute to 100 mL. **CAUTION:** Reaction is exothermic.
10.12 Sulfuric acid - concentrated (18 M), ACS grade, Fisher no. A300. **CAUTION:** Sulfuric acid is corrosive.
10.13 50% Sulfuric acid solution (1:1 v/v) - Carefully pour 50 mL of concentrated sulfuric acid into 50 mL of water. **CAUTION:** Reaction is exothermic.
10.14 Hydrochloric acid - concentrated, ACS grade or equivalent, Fisher no. A508. **CAUTION:** Hydrochloric acid is corrosive.
10.15 Sodium sulfate - granular, anhydrous, Fisher no. S415. Purify by heating at 400-500°C for at least 4 hours.
10.16 Acidified sodium sulfate for method 8151 - Slurry 100 g of purified sodium sulfate with enough diethyl ether to just cover the solid; then add 0.1 mL of concentrated sulfuric acid and mix thoroughly. Remove the ether under vacuum. Mix 1 g of the resulting solid with 5 mL of reagent water and measure the pH. The pH must be less than 4. Store the remaining solid at 130°C
10.17 Sand - washed sea sand, Fisher no. S25. Purify by heating at 400-500°C for at least 4 hours.
10.18 Sodium chloride - analytical reagent grade, Mallinckrodt no. 7581.

10.19 Copper - granular or powder, copper should be reactive, as evidenced by a bright shiny appearance, JT Baker no. 1720-01.

10.20 Florisil - granular, 60-100 mesh, Fisher F100. Prepared by heating at 400-500°C for at least 4 hours.

10.21 GPC Calibration Standards - consisting of corn oil, phthalate, methoxychlor, perulene, and sulfur; Vitron Scientific no. CLP-340.

10.22 Diazald, N-methyl-N-nitroso-p-toluenesulfonamide - high purity grade, Aldrich no. D2,800-0.

10.23 Ethoxyethoxy ethanol (Carbitol, diethylene glycol monoethyl ether), reagent grade, Aldrich no. E455-0.

10.24 Potassium hydroxide - pellets, NF/FCC grade, Mallinckrodt no. 6976. **CAUTION:** Sodium hydroxide is caustic.

10.25 Potassium hydroxide solution (37% w/v). Dissolve 37 g of potassium hydroxide (KOH) in water and dilute to 100 mL. **CAUTION:** Reaction is exothermic.

10.26 Potassium hydroxide solution (12% w/v). Dilute one volume of 37% KOH solution with two volumes of water. For example, dilute 30 mL KOH solution with 60 mL of water.

11.0 EXTRACTION PROCEDURES

Refer to the summary of extraction procedures, Attachment 2 of this SOP.

11.1 SEPARATORY FUNNEL LIQUID-LIQUID EXTRACTION (METHOD 3510C)

11.1.1 Measure 1000 mL of sample using a 1000-mL graduated cylinder and pour into a labeled 2000-mL separatory funnel. If 1000 mL of sample is not available, use all of the sample and record the volume. Also measure and pour 1000 mL portions of organic-free water into separatory funnels for the method blank, blank spike, and blank spike duplicates.

NOTE: If high analyte concentrations are anticipated, a smaller sample volume may be measured and diluted to 1000 mL with water. Record the volume used for later calculations of dilution factor and analyte concentrations.

11.1.2 Using a 1.0-mL syringe, add 1.0 mL (50 µL for 8015 methods) of the appropriate surrogate spiking solution to each sample, blank and QC sample in the analytical batch and mix well. For the blank spike and blank spike duplicate samples, add 1.0 mL of spiking solution to 1000 mL aliquots of blank reagent water.

11.1.3 For methods 8081, 8082, and 8270, check the pH of the sample(s) with pH paper. If necessary, adjust the pH using 50% (1:1 v/v) sulfuric acid solution or 10 N sodium hydroxide, to the following pH values:

- Method 8081 - between 5 and 9 (inclusive).
- Method 8082 - between 5 and 9 (inclusive).
- Method 8270 - first set of extractions ≤2, second set of extractions ≥11.

Samples for methods 8015 and 8310 do not require checking or adjustment.

11.1.4 For each sample, use 60 mL of methylene chloride (60 mL of hexane for method 8015D) to rinse the sample bottle and the graduated cylinder. Transfer to the separatory funnel. Seal and shake the separatory funnel vigorously for two minutes with periodic venting to release excess pressure.

CAUTION: Organic solvents can create excessive pressure very rapidly; therefore, venting should be done immediately after the separatory funnel has been sealed and shaken once. The separatory funnel is vented into a hood to avoid exposure of the analyst to solvent vapors.

11.1.5 Allow the organic layer (*i.e.* the bottom layer if methylene chloride, top layer if hexane) to separate from the water phase. The layers should be visually separate. Collect the solvent extract in a 500-mL Erlenmeyer flask

NOTE: If the emulsion interface between layers is more than about 1/3 the size of the solvent layer, additional techniques to complete the phase separation must be employed. The optimum technique depends upon the sample and may include slow draining of the solvent, stirring, filtration of the emulsion through glass wool and/or sodium sulfate, or dissolving sodium chloride in the sample.

11.1.6 Repeat the extraction two more times using fresh 60 mL portions of solvent. Combine the three solvent extracts in the Erlenmeyer flask. Combine all extracts in the Erlenmeyer flask.

NOTE: If extracting sample for method 8270, perform three extractions. Then adjust the pH of the sample to ≥11 using 10 N sodium hydroxide and re-extract the sample three more times.

11.1.7 For each sample, assemble a Kuderna-Danish (K-D) concentrator by attaching a 10-mL concentrator tube to a 500-mL evaporator flask. Dry the extract by adding anhydrous sodium sulfate to the Erlenmeyer flask and swirling. If the sodium sulfate appears completely hydrated, add additional amounts. Then pass the extract through a filter funnel, containing a folded filter paper containing some sodium sulfate, into the K-D concentrator. Rinse the Erlenmeyer extract flask with about 20-25 mL of solvent, and pass through the drying funnel into the K-D concentrator. Then rinse the drying funnel with about 15-20 mLs of solvent. Add 2-3 clean boiling chips to the K-D and attach a 3-ball Snyder column. Prewet the Snyder column by adding about 1 mL of solvent to the top of the column.

11.1.8 Place the K-D apparatus on the hot water bath so the concentrator tube is partially immersed in the water. When the volume of extract reaches 1-5 mL, remove the K-D apparatus from the bath and allow to drain and cool for approximately 10 minutes.

NOTE: If a solvent exchange is required (for example, hexane for methods 8015, 8081, 8082, and acetonitrile for method 8310), do not remove the K-D apparatus, pour 50 mL of hexane, or 10 mL of acetonitrile, into the top of the Snyder column, and concentrate the extract back down to 1-5 mL. Then remove the K-D apparatus from the bath and allow to drain and cool.

NOTE: At the proper rate of distillation, the balls in the Snyder column should actively chatter, but the chambers will not flood. The concentration should take 10-20 minutes.

11.1.9 Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1-2 mL of the final solvent. For method 8310, add acetonitrile to a final volume of 10 mL. For methods 8015, 8081, 8082, and 8070, use the nitrogen blowdown apparatus to reduce the extract volume to 1 mL.

11.1.10 If extract requires cleanup, see appropriate cleanup procedure(s), Section 12.0.

11.1.11 Using 1-mL glass syringes with syringe filters, transfer 1 mL of final extracts to labeled autosampler vials for analysis (for method 8310, transfer extracts to HPLC autosampler vials, and an additional 1 mL to GC autosampler vials as a backup). Vials are labeled with the Great Lakes sample number, the analytical method number, the sample cleanup method number (if applicable), the initial volume of the sample, the final extract volume, and the date extracted. Extracts may be colored, but should not contain particulate, cloudiness, or have two layers.

11.2 SEPARATORY FUNNEL LIQUID-LIQUID EXTRACTION AND DERIVATIZATION FOR HERBICIDES (METHOD 8151)

CAUTION: Notify the Inorganics Department that ether will be in use.

11.2.1 Measure 1000 mL of sample using a 1000-mL graduated cylinder and pour into a labeled 2000-mL separatory funnel. If 1000 mL of sample is not available, use all of the sample and record the volume. Also measure and pour 1000 mL portions of organic-free water into separatory funnels for the method blank, blank spike, and blank spike duplicates.

11.2.2 Using a 1.0-mL syringe, add 1.0 mL of appropriate surrogate spiking solution to each sample, blank and QC sample in the analytical batch and mix well. For the blank spike and blank spike duplicate samples, add 1.0 mL of spiking solution to 1000 mL aliquots of blank reagent water. Add 250 g of sodium chloride to each sample and shake to dissolve.

11.2.3 Add approximately 10 mL of cold 50% sulfuric acid to each sample. Check the pH of the sample(s) with pH paper. If necessary, adjust the pH using additional 50% sulfuric acid to ≤2.

11.2.4 For each sample, rinse the sample bottle and graduated cylinder with 120 mL of diethyl ether, and place in the separatory funnel. Seal and shake the separatory funnel vigorously for two minutes with periodic venting to release excess pressure.

CAUTION: Organic solvents can create excessive pressure very rapidly; therefore, venting should be done immediately after the separatory funnel has been sealed and shaken once. The separatory funnel is vented into a hood to avoid exposure of the analyst to solvent vapors.

11.2.5 Allow the ether (top) layer to separate from the water phase. The layers should be visually separate. Drain the water (lower) layer into a clean beaker or Erlenmeyer flask. Collect the ether extract in an Erlenmeyer flask containing some acidified anhydrous sodium sulfate.

NOTE: If the emulsion interface between layers is more than about 1/3 the size of the solvent layer, additional techniques to complete the phase separation must be employed. The optimum technique depends upon the sample and may include slow draining of the solvent, stirring, filtration of the emulsion through glass wool and/or sodium sulfate, or dissolving sodium chloride in the sample.

11.2.6 Pour the aqueous phase back into the separatory funnel. Repeat the extraction two more times using fresh 60 mL portions of ether. Combine all extracts in the Erlenmeyer flask.

11.2.7 For each sample, assemble a Kuderna-Danish (K-D) concentrator by attaching a 10-mL concentrator tube to a 500-mL evaporator flask. Dry the extract by adding additional acidified anhydrous sodium sulfate to the Erlenmeyer flask and swirling. If the sodium sulfate appears completely hydrated, add additional amounts. Sample extracts should be dry prior to methylation or else poor recoveries may be obtained (let sit 1½ to 2 hours). Then pass the extract through a filter funnel, containing a folded filter paper containing some sodium sulfate, into the K-D concentrator. Rinse the Erlenmeyer extract flask with 20-25 mL of ether, and pass through the drying funnel into the K-D concentrator. Then rinse the drying funnel with 15-20 mLs of ether.

11.2.8 Add 2-3 clean boiling chips to the K-D and attach a 3-ball Snyder column. Prewet the Snyder column by adding about 1 mL of solvent to the top of the column. Place the K-D apparatus on the hot water bath so that the concentrator tube is partially immersed in the water.

CAUTION: Diethyl ether is very volatile and flammable.

NOTE: At the proper rate of distillation, the balls in the Snyder column should actively chatter, but the chambers will not flood. The concentration should take 10-20 minutes.

11.2.9 When the volume of extract reaches approximately 1 mL, remove the K-D apparatus from the bath and allow to drain and cool. For each extract, add 0.5 of methanol, 1 mL of hexane, and bring to 4 mL volume with ether.

11 2 10 Assemble the diazomethane bubbler. Add about 10-12 mL of ether to the first test tube. Add 3 mL of ether, 3 mL of ethoxyethoxy ethanol, 4.5 mL of 37% KOH, and 2 scoops (about 0.5 g) of Diazald to the second test tube. Place the exit tube into the concentrator tube containing the sample extract.

CAUTION: Diazomethane is a carcinogen, and can explode under certain conditions - refer to the MSDS

NOTE: These amounts are sufficient for derivatization of two samples. Rinse exit tube with ether between samples.

11 2 11 Apply nitrogen flow at about 10 mL/min to bubble diazomethane through the extract for 10 minutes, or until a yellow color persists.

11 2 12 Dilute the extracts to final volume of 10 mL with hexane.

11.2 13 Using 1-mL glass syringes with syringe filters, transfer 1 mL of final extracts to labeled autosampler vials for analysis. Vials are labeled with the Great Lakes sample number, the analytical method number, the sample cleanup method number (if applicable) the initial volume of the sample, the final extract volume, and the date extracted. Extracts may be colored, but should not contain particulate, cloudiness, or have two layers.

11.3 ULTRASONIC EXTRACTION (METHOD 3550B, except for 8015 WDRO)

11 3 1 Weigh approximately 30 g (*i.e.* 25-35 g) of sample into 500-mL beaker and record the weight to the nearest 0.1 g. Prepare each of the method blank, lab control spike, and matrix spikes using approximately 30 g of sand.

11 3 2 For methods 8081, 8082, 8270 and 8310, add 1.0 mL of the surrogate standard solution to each sample, blank and QC samples. For method 8015 (TPHD), add 50 µL of the surrogate standard solution to each sample blank and QC samples. Add 1.0 mL of the matrix spike solution to aliquots of the sample chosen for matrix spike and matrix spike duplicate

11.3.3 Add 100 mL of extraction solvent (methylene chloride for methods 8270, 8310 and 8015 TPHD; 1:1 (v/v) acetone/methylene chloride for methods 8081 and 8082) to each beaker, measuring volumes of solvent using dispenser or volume markings on beakers.

11 3 4 Place the bottom surface of the tip of the disrupter horn below the surface of the solvent, but above the solids layer. Extract ultrasonically for 3 minutes, with the output control knob set at 10 (full power) and with the mode switch on Pulse (not continuous), and percent-duty cycle knob set at 50% (*i.e* energy on 50% of the time and off 50% of the time).

11.3 5 Decant the extract and filter it through a filter funnel containing a folded filter paper and anhydrous sodium sulfate into a Kuderna-Danish (K-D) apparatus.

11 3 6 Repeat the extraction two more times with two additional 100 mL portions of solvent. After each extraction, filter the extract through the sodium sulfate filter into the K-D apparatus. If the sodium sulfate appears completely hydrated, replace the filter paper and use fresh sodium sulfate. Rinse the filter funnel with about 15-20 mLs of solvent.

11.3.7 Add 2-3 clean boiling chips to the K-D and attach a 3-ball Snyder column. Prewet the Snyder column by adding about 1 mL of solvent to the top of the column. Place the K-D apparatus on the hot water bath so that the concentrator tube is partially immersed in the water.

11.3.8 When the volume of extract reaches 1-5 mL, remove the K-D apparatus from the bath and allow to drain and cool for approximately 10 minutes.

NOTE: If a solvent exchange is required (for example, hexane for methods 8015, 8081, 8082, and acetonitrile for method 8310), do not remove the K-D apparatus, pour 50 mL of hexane, or 10 mL of acetonitrile, into the top of the Snyder column, and concentrate the extract back down to 1-5 mL. Then remove the K-D apparatus from the bath and allow to drain and cool.

NOTE: At the proper rate of distillation, the balls in the Snyder column should actively chatter, but the chambers will not flood. The concentration should take 10-20 minutes.

11.3.9 Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1-2 mL of the final solvent. For method 8310, bring extract to a final volume of 10 mL with acetonitrile. For methods 8015, 8081, 8082, and 8270, use the nitrogen blow-down apparatus to reduce extract volume to 1 mL.

11.3.10 If extract requires cleanup, see appropriate cleanup procedure(s), Section 12.0.

11.3.11 Using 1-mL glass syringes with syringe filters, transfer 1 mL of final extracts to labeled autosampler vials for analysis (for method 8310, transfer extracts to HPLC autosampler vials, and an additional 1 mL to GC autosampler vials as a backup). Vials are labeled with the Great Lakes sample number, the analytical method number, the sample cleanup method number (if applicable), the initial volume of the sample, the final extract volume, and the date extracted. Extracts may be colored, but should not contain particulate, cloudiness, or have two layers.

11.4 WDRO SOIL SAMPLE PRESERVATION AND ULTRASONIC EXTRACTION (8015 WDRO)

NOTE: Hexane must be added to soil containers within 72 hours of collection.

11.4.1 Weigh the sample jar and subtract the empty weight to determine the actual soil weight. Record the sample weight in the soil preservation logbook. If the sample weight in a 2 oz jar is >35 grams, or in a 4 oz jar is >70 grams, indicate this in the logbook.

11.4.2 Add hexane to the sample jar in a 1:1 ratio of mL hexane to grams of sample. (If the sample weight is less than 25 g, then add 25 mL hexane.) Add an amount of anhydrous sodium sulfate equal to the sample weight to the sample jar. Spike the sample with 50 µL of WDRO surrogate standard solution. Cap and mix by shaking briefly. Store sample jars in the sample refrigerator until ready for extraction (Section 11.3.3 and following).

11.4.3 WDRO soil sample jars are placed in an water bath and sonicated for 20 minutes. After sonication, the sample extract is filtered through a filter funnel containing a folded piece of filter paper and sodium sulfate into a 200-mL Zymark concentrator tube.

11.4.4 Approximately 30 mL of fresh hexane is added to the sample jar. The jar is capped tightly, placed again in the ultrasonic water bath and sonicated for 20 minutes. After sonication, the contents of the jar are filtered through the filter funnel into the same concentrator tube as the first filtrate. The sample jar is rinsed with about 20-25 mLs of hexane, which is then filtered through the filter funnel.

11.4.5 The concentrator tubes containing the sample extracts are placed into the Turbo Vap II automatic evaporative concentrator, and the evaporation cycle started. The Turbo Vap II automatically concentrates the extract to 1 mL, and then audibly signals that the cycle is complete.

11.4.6 Using a glass Pasteur pipet, transfer 1 mL of final extracts to labeled autosampler vials for analysis. Vials are labeled with the Great Lakes sample number, the analytical method number, the sample cleanup method number (if applicable), the initial volume of the sample, the final extract volume, and the date extracted. Extracts may be colored, but should not contain particulate, cloudiness, or have two layers.

11.5 ULTRASONIC EXTRACTION AND DERIVATIZATION FOR HERBICIDES (METHOD 8151)

CAUTION: Notify the Inorganics Department that ether will be in use.

11.5.1 For each sample, weigh approximately 30 g (*i.e.* 25-35 g) of sample into a 500-mL beaker and record the weight to the nearest 0.1 g. (For wipe samples, weigh the entire wipe.) Prepare each of the method blank, lab control spike, and matrix spikes using approximately 30 g of sand. Adjust the pH of sample to ≤2 with concentrated hydrochloric acid.

11.5.2 Add 100 µL of the surrogate standard solution to each sample, blank and QC samples. Add 100 µL of the matrix spike solution to aliquots of the sample chosen for matrix spike and matrix spike duplicate.

11.5.3 Add 100 mL of methylene chloride to each beaker, measuring volumes of solvent using dispenser or volume markings on beakers.

11.5.4 Place the bottom surface of the tip of the disrupter horn below the surface of the solvent (approximately 0.5 inches), but above the solids layer. Extract ultrasonically for 3 minutes, with the output control knob set at 10 (full power) and with the mode switch on Pulse (not continuous) and percent-duty cycle knob set at 50% (*i.e.* energy on 50% of the time and off 50% of the time).

11.5.5 Place the extract in an Erlenmeyer flask. Repeat the extraction two more times with fresh 100 mL portions of methylene chloride. Combine extracts.

11.5.6 For each sample, assemble a Kuderna-Danish (K-D) concentrator by attaching a 10-mL concentrator tube to a 500-mL evaporator flask. Dry the extract by adding acidified anhydrous sodium sulfate to the Erlenmeyer flask and swirling. If the sodium sulfate appears completely hydrated, add additional amounts. Allow the drying agent to remain in contact with the extract for at least 2 hours. Then pass the extract through a filter funnel, containing a folded filter paper containing some acidified anhydrous sodium sulfate, into a K-D concentrator. Rinse the Erlenmeyer extract flask with about 20-25 mL of solvent, and pass through the funnel into the K-D concentrator. Then rinse the funnel with about 15-20 mL of solvent.

11.5.7 Add 2-3 clean boiling chips to the K-D and attach a 3-ball Snyder column. Prewet the Snyder column by adding about 1 mL of methylene chloride to the top of the column. Place the K-D apparatus on the hot water bath so that the concentrator tube is partially immersed in the water.

11.5.8 When the volume of extract reaches approximately 5 mL, remove the K-D apparatus from the bath and allow to drain and cool.

NOTE: At the proper rate of distillation, the balls in the Snyder column should actively chatter, but the chambers will not flood. The concentration should take 10-20 minutes.

11.5.9 For each sample, place the concentrated extract into a 125-mL separatory funnel. Extract using 15 mL of 12% potassium hydroxide. Shake vigorously for 2 minutes.

CAUTION: Organic solvents can create excessive pressure very rapidly; therefore, venting should be done immediately after the separatory funnel has been sealed and shaken once. The separatory funnel is vented into a hood to avoid exposure of the analyst to solvent vapors.

11.5.10 Drain the organic (lower) layer into a clean beaker. Drain the aqueous layer into an Erlenmeyer flask. Pour the organic layer back into the separatory funnel. Extract twice more using fresh 15 mL portions of 12% potassium hydroxide. Combine aqueous extracts.

11.5.11 Adjust the pH of the aqueous extract to ≤2 with cold 50% sulfuric acid. Place in a clean 125-mL separatory funnel and extract using 40 mL of diethyl ether. Shake vigorously for 2 minutes.

CAUTION: Addition of sulfuric acid to the sample may cause an exothermic reaction. Vent the separatory funnel to release pressure.

11.5.12 Drain the aqueous (lower) layer into a clean beaker. Drain the ether extract layer into an Erlenmeyer flask. Pour the aqueous layer back into the separatory funnel. Extract twice more using fresh 20 mL portions of ether. Combine ether extracts.

11.5.13 For each sample assemble a Kuderna-Danish (K-D) concentrator by attaching a 10-mL concentrator tube to a 500-mL evaporator flask. Dry the extract by adding acidified anhydrous sodium sulfate to the Erlenmeyer flask and swirling. If the sodium sulfate appears completely hydrated, add additional amounts. Allow the drying agent to remain in contact with the extract for at least 2 hours. Sample extracts should be dry prior to methylation or else poor recoveries may be obtained. Then pass the extract through a filter funnel, containing a folded filter paper containing some sodium sulfate, into a K-D concentrator. Rinse the Erlenmeyer extract flask with about 20-25 mL of solvent, and pass through the funnel into the K-D concentrator. Then rinse the funnel with about 15-20 mLs of solvent.

11.5.14 Add 2-3 clean boiling chips to the K-D and attach a 3-ball Snyder column. Prewet the Snyder column by adding about 1 mL of ether to the top of the column. Place the K-D apparatus on the hot water bath so that the concentrator tube is partially immersed in the water.

CAUTION: Diethyl ether is very volatile and flammable.

11.5.15 When the volume of extract reaches approximately 1 mL, remove the K-D apparatus from the bath and allow to drain and cool.

11.5.16 Assemble the diazomethane bubbler. Add about 10-12 mL of ether to the first test tube. Add 3 mL of ether, 3 mL of ethoxyethoxy ethanol, 4.5 mL of 37% KOH, and 2 scoops (about 0.5 g) of Diazald to the second test tube. Place the exit tube into the concentrator tube containing the sample extract.

CAUTION: Diazomethane is a carcinogen, and can explode under certain conditions - refer to the MSDS.

NOTE: These amounts are sufficient for derivatization of two samples. Rinse exit tube with ether between samples.

11.5.17 Apply nitrogen flow at about 10 mL/min to bubble diazomethane through the extract for 10 minutes, or until a yellow color persists.

11.5.18 Dilute the extracts to final volume of 10 mL with hexane.

11.5.19 Using 1-mL glass syringes with syringe filters, transfer 1 mL of final extracts to labeled autosampler vials for analysis. Vials are labeled with the Great Lakes sample number, the analytical method number, the sample cleanup method number (if applicable), the initial volume of the sample, the final extract volume, and the date extracted. Extracts may be colored, but should not contain particulate, cloudiness, or have two layers.

11.6 WASTE DILUTION (METHOD 3580A)

11.6.1 Depending on the determinative method requested for the waste dilution sample, a small amount (1-2 g) of sample is mixed in a beaker with approximately 10 mLs of the appropriate solvent. If the sample dissolves in the solvent, the sample can then proceed through the waste dilution procedure (11.4.2). If the sample does not dissolve in the appropriate solvent, then the sample must be extracted as either a water or a soil, depending upon the nature of the sample.

11.6.2 Weigh approximately 1 g (0.9 to 1.1 g) of sample into a 250-mL beaker, add 1 mL of the waste dilution surrogate spike solution, and bring to 10 mL final volume with the solvent appropriate for the determinative method. Mix until the sample is fully dissolved. The method blank is 1 mL of the waste dilution surrogate spike solution and 9 mL of solvent mixed in a 250-mL beaker. The blank spike and duplicate are each made by mixing 1 mL of the appropriate spiking solution, 1 mL of the waste dilution surrogate spiking solution, and 8 mL of solvent in 250-mL beakers.

11.6.3 If the sample solution requires cleanup, see the appropriate cleanup procedure(s), Section 12.0

11.6.4 Using 1-mL glass syringes with syringe filters, transfer 1 mL of final extracts to labeled autosampler vials for analysis (for method 8310, transfer extracts to HPLC autosampler vials, and an additional 1 mL to GC autosampler vials as a backup). Vials are labeled with the Great Lakes sample number, the analytical method number, the sample cleanup method number (if applicable), the initial volume of the sample, the final extract volume, and the date extracted. Extracts may be colored, but should not contain particulate, cloudiness, or have two layers.

12.0 CLEANUP PROCEDURES

12.1 SULFURIC ACID CLEANUP (METHOD 3665A)

12.1.1 This cleanup procedure is applicable to sample extracts that are to be analyzed for PCB's only and which contain observable hydrocarbon contamination, or that have been analyzed and have been shown to contain interfering hydrocarbon contamination. This method uses sulfuric acid for the removal of these substances. The method cannot be used to cleanup extracts for other target analytes, as it will destroy most organic chemicals including the pesticides Aldrin, Dieldrin, Endrin, Endosulfan (I and II), and Endosulfan sulfate.

12.1.2 The cleanup procedure is performed in a 4-mL clear glass vial with a Teflon-lined screw cap. One mL of hexane extract and and 1 mL of concentrated sulfuric acid are added to the vial, the vial is tightly capped, and then vigorously shaken by hand or on a mechanical shaker for 5 minutes. The solution is then allowed to separate into acid (lower) and hexane (upper) layers. Complete separation of the layers may take between 5 minutes and several hours. Separation can sometimes be expedited by centrifuging the solution. After the layers

completely separate, transfer the hexane layer to a new autosampler vial for sulfur cleanup, and proceed with Section 12.2.

12.2 SULFUR CLEANUP (METHOD 3660B)

12.2.1 This cleanup procedure is applicable to sample extracts that are suspected to contain dissolved sulfur, or extracts that have been analyzed and have been shown to contain dissolved sulfur. This procedure uses copper powder for the removal of dissolved sulfur.

12.2.2 The cleanup procedure is performed directly in the sample extract autosampler vial. Granular copper (20-30 mesh, about 2 g) is added to the 1 mL of extract in the vial to fill about ¼ of the vial volume. The vial is capped and shaken vigorously by hand or on a mechanical shaker for 5 minutes. If the shiny surface of the granular copper turns completely black the extract may still contain dissolved sulfur, in which case the extract should be transferred to a new vial, and the procedure repeated with a fresh portion of copper. If the copper has not turned completely black, transfer the cleaned extract to a new labeled autosampler vial for analysis, through a syringe filter attached to a 1-mL Luer-Lok syringe.

12.3 FLORISIL CLEANUP (METHOD 3620B)

CAUTION: Notify the Inorganics Department that ether will be in use

12.3.1 This cleanup procedure is applicable to sample extracts that are to be analyzed for PCB's and/or organochlorine pesticides, and which contain observable hydrocarbon contamination, or that have been analyzed and have been shown to contain interfering hydrocarbon contamination. This procedure is intended only for the cleanup of samples, and not for fractionation. Standardized Florisil must be used for fractionation.

12.3.2 Add approximately 20 g of dried Florisil to a 20 mm glass chromatography column. Settle the Florisil by gently tapping the column. Add anhydrous sodium sulfate to the top of the Florisil to form a layer 1 to 2 cm deep.

12.3.3 Pre-elute the column with 60 mL of hexane and discard the eluate. Drain the column until the sodium sulfate layer is nearly exposed (*i.e.* solvent drained down to the top of the layer). Quantitatively transfer the sample extract onto the column, completing the transfer using two 1-2 mL rinses with hexane

12.3.4 Place a 500-mL K-D flask equipped with a clean 10-mL concentrator tube under the chromatographic column. Drain the column into the flask until the sodium sulfate layer is nearly exposed. Elute the column with 200 mL of 6% diethyl ether in hexane (v/v), using a drip rate of about 5 mL/minute; followed by 200 mL of 15% ether/hexane, and 200 mL of 50% ether/hexane.

NOTE: If the sample is to be analyzed only for PCB's, then only elute with 200 mL of 50% diethyl ether in hexane.

12.3.5 Add 2-3 clean boiling chips to the K-D and attach a 3-ball Snyder column. Prewet the Snyder column by adding about 1 mL of hexane to the top of the column. Place the K-D apparatus on the hot water bath so that the concentrator tube is partially immersed in the water. When the volume of extract reaches 1-5 mL, remove the K-D apparatus from the bath and allow to drain and cool for approximately 10 minutes.

CAUTION: Diethyl ether is very volatile and flammable.

NOTE: At the proper rate of distillation, the balls in the Snyder column should actively chatter, but the chambers will not flood. The concentration should take 10-20 minutes.

12.3.6 Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1-2 mL of the final solvent. If necessary, use the nitrogen blowdown apparatus to reduce the extract volume to 1 mL.

12.3.7 Using 1-mL glass syringes with syringe filters, transfer 1 mL of final extracts to labeled autosampler vials for analysis (for method 8310, transfer extracts to HPLC autosampler vials, and an additional 1 mL to GC autosampler vials as a backup). Vials are labeled with the Great Lakes sample number, the analytical method number, the sample cleanup method number (if applicable), the initial volume of the sample, the final extract volume, and the date extracted. Extracts may be colored, but should not contain particulate, cloudiness, or have two layers

12.4 GEL PERMEATION CLEANUP (METHOD 3640A)

12.4.1 Gel permeation chromatography (GPC) is a size exclusion cleanup procedure using organic solvents and hydrophobic gels to separate molecules of different sizes. For example, GPC cleanup can be used to remove lipids, polymers, copolymers, proteins, and natural resins from samples.

12.4.2 Set the flow rate to 5 mL/min of methylene chloride. Switch the flow transfer valve for the eluent to flow to waste.

12.4.3 For each sample, prepare a Kuderna-Danish (K-D) apparatus for collection of sample eluent.

12.4.4 Retention times of the components of the GPC calibration standards must be checked at least once per week when running this cleanup procedure. Flush and load the sample loop using 1 mL of standard solution. Inject and start the chart recording. Determine and record the retention times for each component. Note elution times for the end of the phthalate peak and the beginning of the sulfur peak.

12.4.5 For cleanup of samples, flush and load the sample loop using 1 mL of sample. Inject and start the chart recording. Immediately after the elution time of phthalate, switch the flow transfer valve for eluent to the outlet line leading to the K-D. Just before the elution time of sulfur, switch the valve to transfer flow to waste. Allow sufficient time for sulfur compounds to elute before injection of another sample.

12.4.6 Add 2-3 clean boiling chips to the K-D and attach a 3-ball Snyder column. Prewet the Snyder column by adding about 1 mL of methylene chloride to the top of the column. Place the K-D apparatus on the hot water bath so that the concentrator tube is partially immersed in the water. When the volume of extract reaches 1-5 mL, remove the K-D apparatus from the bath and allow to drain and cool for approximately 10 minutes.

NOTE: At the proper rate of distillation, the balls in the Snyder column should actively chatter, but the chambers will not flood. The concentration should take 10-20 minutes.

NOTE: If a solvent exchange is required (for example, hexane for methods 8081 and 8082), do not remove the K-D apparatus, pour 50 mL of hexane into the top of the Snyder column, and concentrate the extract back down to 1-5 mL. Then remove the K-D apparatus from the bath and allow to drain and cool.

12.4.7 Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1-2 mL of the final solvent. If necessary, use the nitrogen blowdown apparatus to reduce the extract volume to 0.5 mL.

12.4.8 Using 1-mL glass syringes with syringe filters, transfer 1 mL of final extracts to labeled autosampler vials for analysis. Vials are labeled with the Great Lakes sample number, the analytical method number, the sample cleanup method number (if applicable), the initial volume of the sample, the final extract volume, and the date extracted. Extracts may be colored, but should not contain particulate, cloudiness, or have two layers.

13.0 MAINTENANCE AND TROUBLESHOOTING

Glassware should be cleaned appropriately (see Section 4.0) to avoid sample contamination. Equipment should be kept clean and maintained to avoid sample contamination and assure proper operation

14.0 REFERENCES

14.1 EPA Method 3500B: Organic Extraction and Sample Preparation.
14.2 EPA Method 3510C: Separatory Funnel Liquid-Liquid Extraction.
14.3 EPA Method 3550B: Ultrasonic Extraction.
14.4 EPA Method 3580A: Waste Dilution.
14.5 EPA Method 3620B: Florisil Cleanup.
14.6 EPA Method 3660B: Sulfur Cleanup.
14.7 EPA Method 3665A: Sulfuric Acid/Permanganate Cleanup.
14.8 EPA Method 8015B: Nonhalogenated Organics Using GC/FID.
14.9 EPA Method 8081A: Organochlorine Pesticides by Gas Chromatography.
14.10 EPA Method 8082: Polychlorinated Biphenyls by Gas Chromatography.
14.11 EPA Method 8270C: Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS).
14.12 EPA Method 8310: Polynuclear Aromatic Hydrocarbons.
14.13 EPA Method 8151 Chlorinated Herbicides by GC Using Methylation or Pentafluorobenzylation Derivatization
14.14 Modified DRO – Method for Determining Diesel Range Organics (Wisconsin DNR).
14.15 Great Lakes Analytical Quality Assurance Program manual.
14.16 Great Lakes Analytical Chemical Hygiene Plan.
14.17 Great Lakes Analytical SOP for Login Department.
14.18 Great Lakes Analytical SOP for Hazardous Sample Management
14.19 Gel Permeation Chromatography Cleanup System Operator's Guide, Waters Chromatography Division, Millipore Corporation.

15.0 DEFINITIONS

See References.

ATTACHMENT 1

SEMIVOLATILES WATER/SOIL EXTRACTION LOG **Page x of 100**

Extraction Method _____ Analytical Method _____

Date Extracted _____ by _____ Sample Matrix _____

Date Concentrated _____ by _____ Date Completed _____ by _____

Extraction Solvent _____ Lot _____ Final Solvent _____ Lot _____ by ____

Surrogate Spike Solution No. _____

Matrix Spike Solution No. _____ **BATCH No.** _____

	Client or ID	Sample No	Sample Size (mL/g)	Surrogate Volume (mL)	Spike Volume (mL)	pH Adjustment	Solvent Exchange	Final Volume (mL)	Comments/ Cleanups
1									
2									
3									
4									
5									
6									
7									
8									
9									
10									
11									
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GREAT LAKES ANALYTICAL

ATTACHMENT 2

EXTRACTION SUMMARY TABLE

[redacted]	8015D-DR	8015T-TPH-D		8081/8082-Pesticides & PCBs		8151-Herbicides		8270-SVOC		8310-PNA	
Sample Matrix	Aqueous	Aqueous	Solid	Aqueous	Solid	Aqueous	Solid	Aqueous	Solid	Aqueous	Solid
Sample Volum0e/Weight	1 L	1 L	30 g	1 l	30 g	1 L	30 g	1 L	30 g	1 L	30 g
Sample Preservative	HCl	none		none		none		none		none	
Surrogate Volume	50 µL	50 µL		1 Ml		1 mL		1 mL		1 mL	
pH	NA	NA		5-9		≤ 2	≤ 2	1) ≤ 2 2) · 11	NA	NA	
Extraction Solvent	Hexane	$MeCl_2$		$MeCl_2$	1.1 Acetone - $MeCl_2$	Diethyl ether	1) $MeCl_2$ 2) KOH 3) Ether	$MeCl_2$		$MeCl_2$	
Extraction Solvent Volume, mL (Replicates)	60 × 3	60 × 3	100 × 3	60 × 3	100 × 3	120, 60 · 2	1) 100 × 3 2) 15 × 3 3) 40. 20×2	1) 60 × 2 2) 60 · 2	100 × 3	60 × 3	100 × 3
Solvent Exchange or Final Solvent	none	Hexane		Hexane		Hexane		none		Acetonitrile	
Volume Solvent Exchange Added	NA	50 mL		50 mL		NA		NA		10 mL	
Nitrogen Blowdown	Yes	Yes		Yes		No		Yes		No	
Extract Final Volume	1 mL	1 mL		1 mL		10 mL		1 mL		10 mL	
Notes						Derivatize with diazomethane		Two extractions at each pH		Fill an additional autosampler vial	

Standard Operating Procedure for Polychlorinated Biphenyls by Gas Chromatography:

Capillary Column Method

GREAT LAKES ANALYTICAL

STANDARD OPERATING PROCEDURE

FOR

POLYCHLORINATED BIPHENYLS BY GAS CHROMATOGRAPHY:

CAPILLARY COLUMN METHOD

GLA 8082 BG

Revision 1.0

Approved By:

Department Manager _____ Date: 10-27-98

Quality Assurance Manager: _____ Date: 10/27/98

Laboratory Manager: _____ Date: 10-27-98

1.0 APPLICABILITY

This standard procedure (SOP) provides instructions for the analysis of polychlorinated biphenyls (PCBs) and related compounds by capillary gas chromatography (GC). This SOP is an interpretation of EPA method 8082. Samples are extracted according to Great Lakes Analytical (GLA) SOP 3500 BG. This SOP is to be used in conjunction with the analysts' in-laboratory training, the Great Lakes Analytical Chemical Hygiene Plan (CHP), and the Great Lakes Analytical Quality Assurance Program.

1.1 MATRICES

This SOP may be used for extracts of aqueous, soil/sediment, solid waste, and non-aqueous solvent-soluble waste samples. Use method 8081 for samples for organochlorine pesticide analysis. If the matrix of these samples were environmentally degraded (*i.e.* "weathered"), pattern recognition of these analytes may require more detailed study.

1.2 REGULATORY APPLICABILITY

40 CFR 121

2.0 SUMMARY

Samples for PCB analysis are extracted with organic solvents (aqueous samples using separatory funnel liquid-liquid extraction, soil/sediment samples using ultrasonic extraction, see GLA SOP 3500 BG, sections 11.1 and 11.3).

Extracts are analyzed by capillary gas chromatography with electron capture detection (ECD). The GC is standardized to determine the recovery and limits of detection for the analytes of interest. Sample concentrations are determined by comparison to standard responses. Quantitative analysis is achieved through measurements of peak heights or integrations of peak areas.

This method is used to determine the concentrations of PCBs as Aroclors (mixtures). Compounds that can be detected by this method include: Aroclors 1016, 1221, 1232, 1242, 1248, 1254, and 1260, 2-chlorobiphenyl, 2,3-dichlorophenyl, and the various isomers (congeners) of tri-, tetra-, penta-, hexa-, hepta-, and nona-chlorobiphenyls

3.0 SAFETY

3.1 GENERAL

This SOP does not address all safety issues associated with its use. A reference file of material safety data sheets (MSDS's) is available to all personnel, along with the Great Lakes Analytical Chemical Hygiene Plan

The toxicity or carcinogenicity of each reagent used in this SOP has not been precisely determined, however, each chemical should be treated as a potential health hazard. Exposure to these chemicals should be reduced to the lowest possible level. Gloves are worn when handling solvents, chemicals, and reagents

3.2 CHEMICAL HYGIENE PLAN

The Great Lakes Analytical Chemical Hygiene Plan (CHP) is designed to establish safe work procedures and minimize exposure to hazardous chemicals encountered in the laboratory. The CHP

provides information to employees regarding potential hazards and training to minimize these hazards.

3.3 COMPRESSED GASES

All compressed gases, except air, can cause suffocation by displacing oxygen. Caution should be exercised when changing compressed gas cylinders. Analysts must wear safety glasses when changing cylinders or working with gas plumbing. All compressed gas cylinders must be secured at all times. A handtruck must be used to transport cylinders. The safety cap is to be in place at all times except when the cylinder is secured and a regulator is in place.

3.4 HAZARDOUS SAMPLES

All samples that are received by the laboratory have the possibility of containing hazardous pollutants. They should be treated with caution at all times. Gloves are worn when handling samples. Also see the Great Lakes Analytical SOP for Hazardous Sample Management.

4.0 INTERFERENCES

4.1 GLASSWARE

Solvents, reagents, glassware, and other sample processing hardware may yield artifacts and/or interferences to sample analysis. All these materials are demonstrated to be free from interferences under the conditions of the analysis by analyzing method blanks. Soap residue (for example, sodium dodecyl sulfate), which causes a basic pH on glassware surfaces, may cause degradation of certain analytes. In general, glassware is washed using Contrad or Alconox detergent, and then rinsed thoroughly with organic-free deionized water, acetone, and finally with methylene chloride.

4.2 PLASTICS

Phthalate esters contaminate many types of products found in the laboratory. Plastics, in particular, should not be used because phthalates are commonly used as plasticizers and are easily extracted from plastic materials. Substantial phthalate contamination may result at any time if consistent quality control is not practiced. Nitrile gloves must be used.

4.3 COEXTRACTED INTERFERENCES

Materials causing interferences may be coextracted from a sample. The extent of matrix interferences varies from sample to sample. If analysis of an extracted sample is prevented due to interferences, further cleanup of the sample extract may be necessary.

4.4 CARRYOVER

Contamination by carryover can occur whenever samples with high concentration and low concentration are analyzed sequentially. The sample syringe or purging device should be rinsed out between samples with solvent to reduce carryover. Whenever an unusually concentrated sample is encountered, it should be followed by an analysis of a solvent blank to check for cross contamination.

4.5 COELUTION

Coelution among the target analytes may cause interference. If this is suspected, standards of the individual analytes may be analyzed and retention times compared.

4.5 SULFUR

The presence of sulfur can result in broad peaks that interfere with the detection of early-eluting analytes. Sulfur contamination should be expected with sediment samples. Since the recovery of sulfur-containing pesticides (*e.g.* endosulfan) is reduced during sulfur cleanup, this compound is determined prior to cleanup.

4.6 INDUSTRIAL CHEMICALS

Other pesticides and industrial chemicals may cause interferences. For example, some coeluting organophosphorous pesticides can be removed using gel permeation chromatography (GPC) cleanup.

5.0 RECORD KEEPING

5.1 INSTRUMENT LOG

Each instrument has an Instrument Log. The instrument identification number and effective dates are written on the front cover. An instrument log is very helpful in tracking problems and is an important troubleshooting guide. Entries in this book include, but are not limited to:

- Installation of the instrument.
- Run parameters for the instrument, autosampler, and data system.
- Instrument and autosampler gas flows.
- All routine and unscheduled maintenance.
- Date and initals of analyst performing work.

5.2 QUALITY CONTROL BOOK

A Quality Control Book is set up for each instrument. It has the instrument identification number on the outside cover. The contents of each book include:

- Copy of the GLA Quality Assurance Program.
- Copies of GLA SOP and source methods.
- Copies of the calibration studies and the internal standard control limits and dates in use.
- Copy of the precision and accuracy study for the method.
- Copies of all method detection limit studies and dates in use.
- Copies of all retention time studies and dates in use.
- Spike and spike duplicate recovery tabulations and control limits.
- Surrogate standard recovery tabulations and control limits.
- Corrective action sheets.

5.3 RUN LOG

The front cover of the Run Log notebook displays:

- Instrument identification number.
- Method number.
- Run log number.
- Effective dates.

In the front of the notebook record:

- Calculations represented with a generic calculation.
- The name and concentration of the surrogate standard.

The following column headings are written at the top of each page:

- Data file name.
- Date.
- Autosampler position.
- Client.
- Full sample number.
- Amount of sample used.
- Matrix type and method.
- Results complete with units.
- Comments
- Analyst.

Each page is initialed and dated. Laboratory notebooks must be neat and legible Mistakes are crossed out with a single line, initialed, and dated. Unused or partial pages are z'ed out

5.4 STANDARD PREPARATION LOG

A log is kept of all standards prepared for the method. Document in the book:

- Analyte, purpose (method, calibration, internal, etc.)
- Supplier
- Lot number
- Initial concentration of the stock solution.
- Expiration date of stock standard - 6 months after the standard has been opened or the date set by manufacturer, whichever is first.
- Initials and date.

Also for working standards

- Volume diluted.
- Volume prepared
- Final concentration.
- Expiration of working standard - 6 months after the standard has been prepared, or when the standard fails Quality Control criteria, whichever is first.
- GLA code for the final solution. The GLA code is a number letter sequence used to track standard preparations within the lab. It consists of the month number and successive letter of the alphabet, starting with "A" at the beginning of each month

6.0 QUALITY CONTROL

6.1 METHOD BLANKS AND SAMPLE SPIKES

For quality control, each water extraction batch contains a method blank (MB), and a blank spike (BS), and a blank spike duplicate (BSD). An analytical batch does not contain more than 20 samples Deionized water is used for water method blanks and spikes. Method spike and duplicate (MS and MSD) samples are analyzed per client request.

Each soil extraction batch contains a method blank (MB), a lab control spike (LCS), a matrix spike (MS), and a matrix spike duplicate (MSD) Clean sand is used for soil method blanks (MB) and spiked blanks (LCS) Samples selected randomly by the LIMS are used for matrix spikes and matrix spike duplicates

Samples are spiked with Aroclor 1016/1260 mixture at a final concentration of 1.0 µg/mL. A surrogate compound is added to all samples, blanks, and spikes in an analytical batch.

A blank spike and blank spike duplicates are associated with all samples. Spikes are run every 20 samples. Spike recoveries for all compounds are documented in tables for yearly tabulation of statistical limits. The spike recoveries must be within the average spike recovery per matrix for a particular compound ± 3 times the standard deviation.

6.2 INSTRUMENT BLANK

The instrument blank verifies that the analytical system is free from contamination - no contamination should be present in the blank above the reporting limit. The instrument blank must be quantitated before samples to verify that the system is "clean" If contamination is found, corrective action must be initiated. For example, samples run in that analysis sequence which contain the same contaminant are reanalyzed with a clean blank to confirm results, or the results flagged to indicate possible contamination.

6.3 CHECK STANDARD

Check standards validate the initial calibration curve and is used to gauge the daily operating condition of the instrument The check standards contain the analytes at concentrations within the calibration range (mid-range) Periodically, a high or low standard may be used for this The peaks are quantitated using the average RF for each compound calculated in the calibration study. Aroclor mixure 1016/1260 is used for initial verification of calibration (CCV).

The recovery of each peak in the check standard must be between 85 and 115 (100 ± 15) % If the average recovery of the entire compound list is 100 ± 15%, then the method is considered "in calibration" for all compounds.

$$Recovery\ (\%) = \frac{calculated\ concentration}{concentration\ analyzed} \times 100$$

A check standard is analyzed once every 10 samples, or every 12 hours The check standard is used to check chromatography for peak shape or co-elution problems The check standard must be quantitated before the samples in the sequence to verify that the samples are being quantitated against a valid calibration Recoveries of all check standard analytes are documented in tables for tabulation of yearly statistical recovery limits.

6.4 SURROGATE STANDARD

Decachlorobiphenyl is employed as a surrogate standard to monitor the efficiency of the procedure. 0.5 µg of surrogate standard is added to all QC and test samples before extraction. The surrogate standard recoveries are tracked from all samples over a year to determine control limits. These limits are defined as the average recovery plus/minus 3 times the standard deviation. Surrogate standard limits are kept in the QC binder and should be posted by the analyst for reference.

6.5 CORRECTIVE ACTION

If a quality control measure fails, corrective action is taken to document steps taken to ensure the accuracy of the data that is reported Examples of when corrective action sheets are filled out are.

- Recovery for check standard fails.
- Contamination was present in the blank and in the sample.
- Recovery for surrogate standard outside of limits.
- Recovery for LCS or matrix spike outside of control limits.

6.6 CONFIRMATION

All client samples with detected levels of any target compound are re-analyzed on an instrument with a confirmation column to verify the presence of the PCB(s). If sensitivity permits, GC/MS method 8270 may be used for confirmation (Full-scan GC/MS will normally require a minimum concentration of 10 ng/µL in the final extract for each single-component compound. GC/MS may not be used for confirmation when concentrations are less than 1 ng/µL in the extracts.) All QC requirements, including calibrations and retention time windows, must be fulfilled for the confirmation analyses. If the confirmation result differs from the original result by more than 40% and there is no evidence of chromatograqphic anomalies or interferences, then the higher value is reported, and the client is notified of the possible problem.

6.7 CHECKLISTS

Checklists are designed to ensure that data being reported by the laboratory have met all of the daily quality control requirements. The analyst documents the status of all quality control requirements for an analytical batch by checking off and filling out Daily Batch Checklists prior to reporting results. If a QC criteria has failed, the analyst must document samples that were affected and whether or not corrective action was taken. See checklists included in this SOP (attachments 1 and 2)

7.0 SAMPLE MANAGEMENT

7.1 The procedure for sample management are detailed in the Great Lakes Analytical SOP for sample receipt into the laboratory. Extraction Logbooks contain records of sample extractions and preparations for analytical batches.

7.2 Sample Schedule. Analysts keep track of sample throughput by using the Laboratory Information Management System (LIMS). The system is checked daily and a hard copy generated. Samples for method 8082 are queued under "EXTR" and "PCBS". The information includes

- Client name.
- Sample numbers
- Project name.
- Matrix.
- Hold time and turnaround time.

8.0 METHOD VALIDATION

8.1 INITIAL CALIBRATION

A calibration study determines the calibration factors (CFs) for analytes that are used for the determination of concentrations of analytes in samples. A series of different concentrations of analytes is compared to respective peak area responses on a chromatogram.

An Aroclor 1016/1260 mixture is used to demonstrate linearity of detection. A minimum of 5 concentration levels are used (a minimum of 5 representative peaks in each chromatogram are used for Aroclor identification and quantitation). A mid-range concentration standard is used for single-point calibration for PCBs other than 1016 and 1260.

Calibration factors (CF) are calculated by tabulating responses of each peak against the known concentrations of the analytes. The curve is considered linear and an average RF may be used if the relative standard deviation (%RSD) is less than 20%. If the %RSD for any compound is greater than

20%, linear regression (not forced through the origin, nor including the origin as a data point) is used to establish the equation of the calibration curve for that particular peak: *peak area = slope × concentration + constant*. Linear regression is valid only if the correlation coefficient (r^2) is 0.99 or greater.

Procedure summary:

- Prepare and analyze a minimum of 5 concentration levels that span the linear range of the system with the lowest level near, but above, the MDL. Add surrogate standard (0.05-1.0 µg/mL of TMX+DCB) to each level.
- For each peak, calculate:
  - $CF = \frac{\text{peak area of analyte}}{\text{concentration of analyte}}$
  - *Average and standard deviation for CFs*
  - $\%RSD = \frac{\text{standard deviation of CFs}}{\text{average RF}} \times 100$

- If the %RSD is less than 20%, the average CF value is used.
- If the %RSD is greater than 20%, a calibration curve is generated using linear regression.
- The correlation coefficient for the linear regression must be 0.99 or greater
- Check standards are analyzed following a calibration study
- Recovery for the check standards must be between 85 and 115%

8.2 DETECTION LIMIT STUDY

This study is performed in accordance with the GLA Quality Assurance Program. This study provides the analyst with the minimum detection limit (MDL) for the instrument and analytes. The MDL is defined as the minimum concentration of the analyte that can be measured and reported at a 99% confidence level. The MDL is equal to the standard deviation of the concentrations determined for 7 matrix spike samples multiplied by the "t value" appropriate for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom. The t value appropriate for 7 samples is 3.143. The calculated MDL must be between 10% and 100% of the concentration of the MDL standard in order for the study to be valid. For example, if 0.20 µg/L of standard is injected, the calculated MDL must be between 0.02 and 0.20 µg/L. A MDL study is performed annually.

Procedure summary

- Analyze 7 replicates of matrix spiked with low level standard (at or below lowest calibration level standard).
- Calculate the standard deviation for the results for the 7 replicates
- Each MDL = standard deviation × 3.143.
- The calculated MDLs must be between 10 and 100% of the MDL standard.

(MDLs for Aroclors should vary in the range of 0.05 to 0.9 µg/L in water, and 57 to 70 µg/kg in soils.)

8.3 RETENTION TIME WINDOW STUDY

The retention time window study is used as a guide for the tentative identification of peaks during sample analyses. A retention time window study is performed when a new column is installed, or annually.

Procedure summary

- Analyze the check standard three times over a 3 day period
- Calculate the average retention time and associated standard deviation for each compound.
- For each compound, retention time window = average retention time ± 3 × standard deviation

- If the instrument is equipped with Enviroquant, enter the retention time windows into the initial calibration tables.

8.4 ACCURACY AND PRECISION STUDY

Each new analyst will perform a series of analyses to establish the ability to generate acceptable precision and accuracy

Procedure summary:
- Analyze 4 replicate standards or spiked extracts.
- Recoveries of each compound must be between 80 and 120%.
- The %RSDs must be less than 20%.

9.0 EQUIPMENT

9.1 Gas chromatograph, consisting of:
- Column oven, electron capture detector (ECD) - Hewlett Packard 5890 or equivalent.
- Sample injector/controller - Hewlett Packard 7672 or equivalent.
- Analytical column - 30 m × 0.53 mm, DB-608 (J&W Scientific, no. 125-6837, or equivalent).
- Data collection and analysis system.

9.2 Glass syringes, various sizes.

9.3 Volumetric flasks, various sizes.

10.0 STANDARDS AND REAGENTS

10.1 STANDARD SOURCES

Standards can be ordered from EPA or A2LA certified companies. These companies include AccuStandard, Restek, Supelco, and Ultra Scientific. Examples of standards include.

10.1.1 Surrogate standard - Restek Surrogate (no. 32000): deca-chlorobiphenyl (200 µg/mL): dilute 250 µL to 100 mL with hexane, for waste dilution samples, dilute 750 µL to 25 mL with hexane.

10.1.2 Spike standard - Mixture of Aroclors 1016 and 1260 at 1.0 µg/mL each

10.1.3 Check standards (1000 µg/mL, in hexane, from Restek) -
- A. Aroclor 1221 (no. 32007)
- B. Aroclor 1232 (no. 32008)
- C. Aroclor 1242 (no. 32009)
- D. Aroclor 1248 (no. 32010)
- E. Aroclor 1254 (no. 32011)
- F. Aroclor 1260 (no. 32012)
- G. Working spike standard - dilute 50 µL of 1000 µg/mL standard(s) to 50 mL with hexane

10.1.3 Calibration standards (1000 µg/mL, in hexane, from Supelco) -
- A. Aroclor 1016 (no. 90123R)
- B. Aroclor 1221 (no. 90124R)
- C. Aroclor 1232 (no. 90125R)
- D. Aroclor 1242 (no. 90126R)
- E. Aroclor 1248 (no. 90127R)
- F. Aroclor 1254 (no. 90128R)
- G. Aroclor 1260 (no. 90129R)

10.2 STANDARD DILUTIONS

Stock and working standards should be kept in a refrigerator between 0 and 10°C when not in use to preserve their integrity.

A useful equation for preparations of diluted standards is:

$$C_2 \times V_2 = C_1 \times V_1$$

C_1 = concentration of the stock standard.
C_2 = desired or calculated concentration of the working standard.
V_1 = volume of the stock standard diluted.
V_2 = volume of working standard prepared.

10.3 STOCK STANDARD

Transfer stock standard to a vial and seal with a Teflon-lined cap. Label this vial with:

- Analyte description
- Manufacturer.
- Lot number
- Concentration.
- Date opened.
- Expiration date.

Place vial in refrigerator. The stock standard expires 3 months after opening, or the expiration date set by the manufacturer, whichever is first. Opening of the standard is documented in the Standard Log

10.4 WORKING STANDARD

Standards are prepared in hexane.

- Determine volumes of stock and working standard required.
- Fill volumetric flask about ¾ full with hexane.
- Add required volume of stock standard.
- Fill volumetric to the mark.
- Cap and invert three times.
- Transfer to vial with "mini-nert" cap.
- Label vial with:
  - Analyte description.
  - Concentration of standard.
  - Date prepared.
  - Purpose (method)
  - Initials.
  - Expiration date
  - GLA code.

The working standard expires 6 months after opening, or when the standard fails QC criteria, whichever is first. Preparation is documented in the Standard Log

NOTE A 5µL aliquot of a 10 ng/µL working standard is equivalent to 50 ng.
10 ng/µL × 5 µL = 50 ng

10.5 REAGENTS

10.5.1 Hexane - pesticide grade or equivalent.
10.5.2 Helium - ultra-high purity grade.
10.5.3 Nitrogen - ultra-high purity grade.

11.0 PROCEDURE

NOTE: Method Validation (section 8.0) must be completed before samples can be analyzed. Samples are analyzed in the same manner as method validation solutions

11.1 ANALYTICAL SEQUENCE

Samples are analyzed in a set referred to as an analysis sequence The sequence begins with verification of instrument calibration, followed by sample extracts interspersed with QC samples. The sequence ends when the set of samples has been injected or when qualitative and/or quantitative QC criteria are exceeded.

11.2 RETENTION TIME WINDOWS

11.2.1 Retention time windows are adjusted daily using the results for each analyte in the check standard.

11.2.2 Tentative identification of an analyte occurs when a peak from a sample extract falls within the daily retention time window All client samples with detected levels of any target compound are re-analyzed on an instrument with a confirmation column (e.g. a dissimilar column) to verify the presence of the analyte(s).

11.3 GAS CHROMATOGRAPHIC OPERATING CONDITIONS

Temperature parameters

Injector:	250°C
Detector:	320°C
Oven program:	140°C for 2 min
	140 to 240°C at 10°C/min (10 min)
	240°C for 8 min
	240 to 260°C at 2.5°C/min (8 min)
	260°C for 1 min
	260 to 280°C at 15°C/min (1.3 min)
	280°C for 10 min

Gas flow

Column	~5 mL/min
Make-up	~50 mL/min

Injection

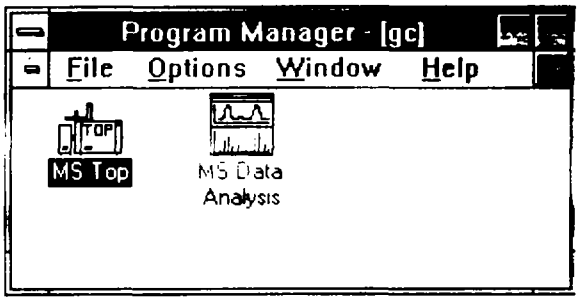
Volume	2 µL splitless

See Figures 1 and 2 for example chromatograms.

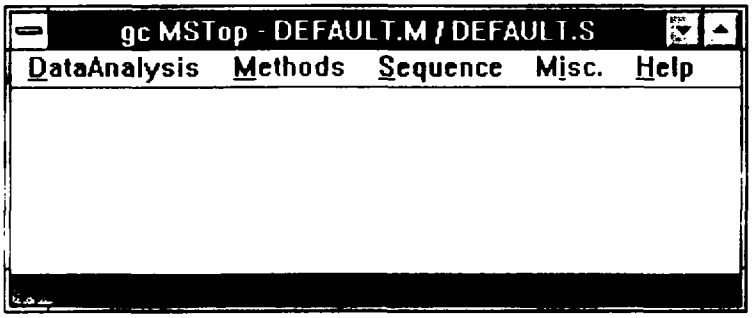
NOTE: Chromatographic conditions may be adjusted to give adequate separation of the characteristic peaks in each Aroclor. Once established, the same operating conditions are used for analysis of samples and standards.

11.4 SETTING UP A SEQUENCE IN ENVIROQUANT

In Program Manager there is a group called GC-Enviroquant or GC/MS-# Using the mouse, double click to open it and there will be an icon that looks like a GC.



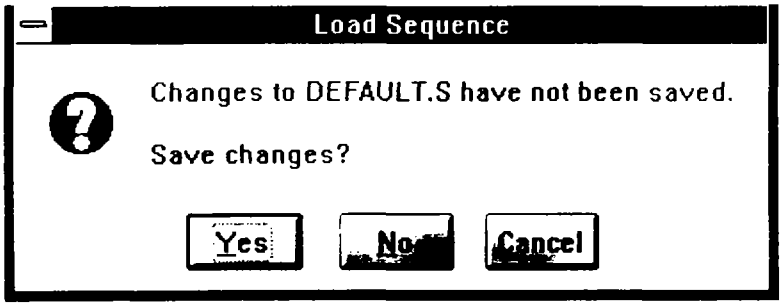
Double click on the GC icon to open it (Note: Actual screen displays "GC Top" and "GC Data Analysis" icons.)



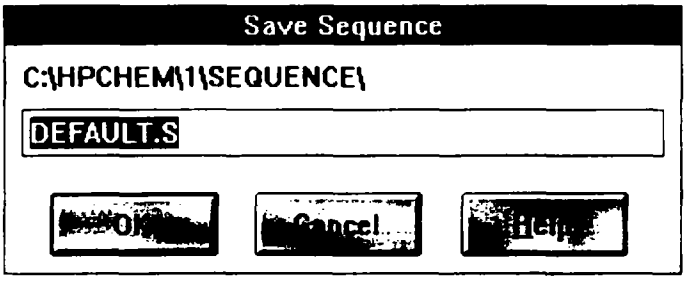
Click on the "Sequence" menu item and drag pointer to "Edit Sample Log Table".
Enter the sample information for each sample including Data File name, Method, and Sample Name.
The sample name is the LIMS information, which will look like:

GLA sample number|PCBS|8082|OK

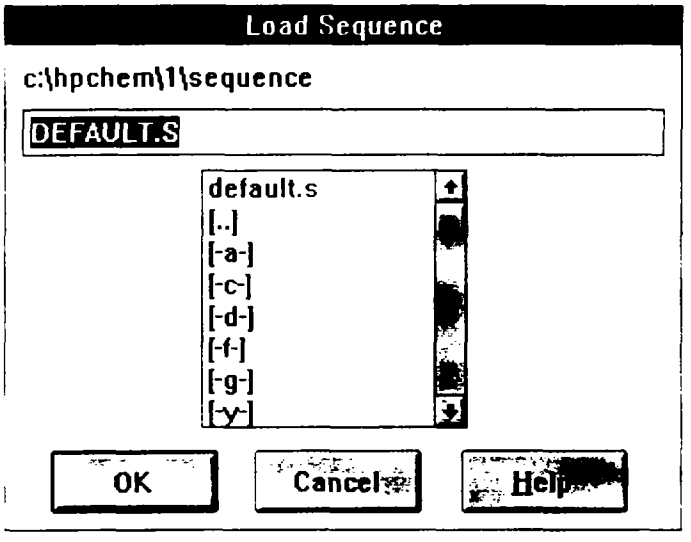
Leave the miscellaneous field empty.
When this is done click on OK.
Go back to the "Sequence" menu and drag to "Load and Run Sequence".



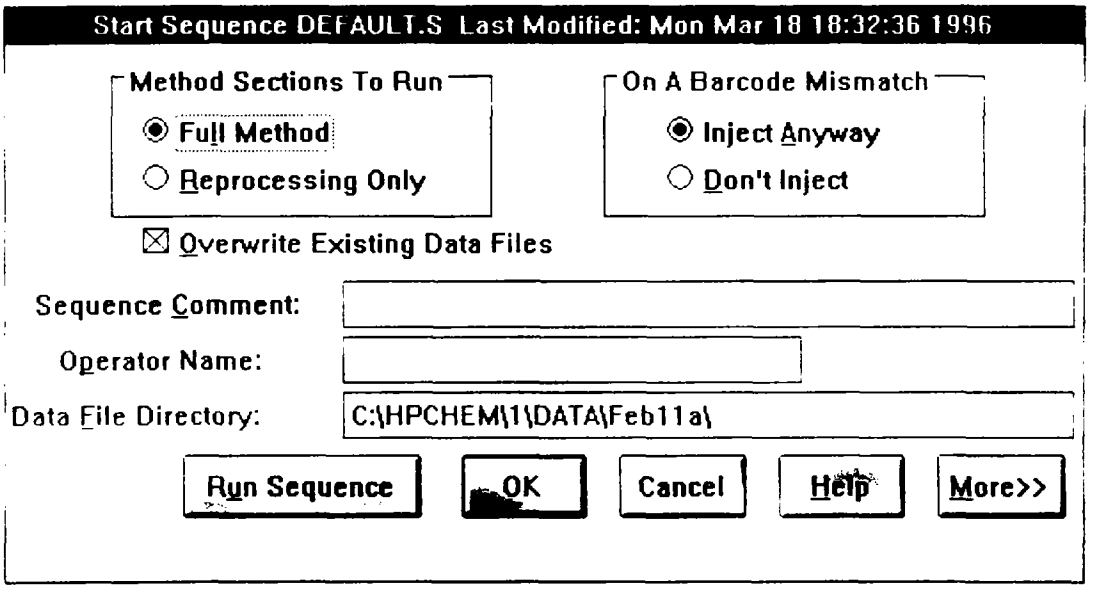
Click on "Yes".



Click on "OK"



Click on "OK".



In the "Method Sections To Run" box, the circle next to "Full Method" should be filled in.
In the "On A Barcode Mismatch" box, the circle next to "Inject Anyway" should be filled in
The box next to "Overwrite Existing Data Files" should be checked.
In the "Operator Name" box, the analyst's initials that are used in LIMS are added.
In the "Data File Directory" field, after \DATA\, enter today's date or if the sequence was interrupted enter today's date with a letter appendage.
Click on Run Sequence.

11.5 QUANTITATION

11.5.1 When analyzing for Aroclors, a minimum of 3 peaks must be chosen for each Aroclor for pattern recognition. At least one of three peaks must be unique to the Aroclor of interest. At least 5 peaks are used for identity of Aroclor 1016/1260 mix. Every attempt should be made to avoid manual integration. If absolutely necessary, it must be performed in a manner which is consistent with the integration of the standards used for calibration. The manipulation of integration parameters in a way that is inconsistent with the integration of standards constitutes fraud and is strictly forbidden.

11.5.2 If the responses exceed the concentration of the upper calibration standard, dilute the extract and reanalyze. If peak detection is prevented by the presence of interferences, further cleanup is required

11.5.3 For reporting compounds that have been confirmed, the concentration of each analyte in the sample is determined by calculating the amount of standard injected, from the peak response, using the average calibration factor (CF) or linear regression calibration curve (section 8.1). These calculations may be done directly by the data collection and analysis software.

For aqueous samples:

Concentrations determined manually -

$$\text{Concentration } (\mu g/L) = \frac{A_x \times V_t \times D \times 1000}{CF \times V_s} \quad \text{or} \quad \frac{(A_x - C) \times V_t \times D \times 1000}{S \times V_s}$$

Where:

A_x = peak area response for the analyte in the sample
CF = average calibration factor.
V_t = volume of total extract (1 mL).
V_s = volume of sample extracted (1000 mL).
D = dilution factor (if no dilution was made, D = 1).
1000 = factor converting liters to milliliters.
C = linear regression constant
S = linear regression slope.

Concentrations determined by software -

$$\text{Concentration } (\mu g/L) = \frac{R_x \times V_t \times D \times 1000}{V_s}$$

Where

R_x = average concentration reported for sample, in µg (divide result by 1000 if concentration reported as mg).
V_t = volume of total extract (1 mL).
V_s = volume of sample extracted (1000 mL)

D = dilution factor (if no dilution was made, D = 1).
1000 = factor converting liters to milliliters.

For soil/solid samples:

Concentrations determined manually -

$$\text{Concentration } (\mu g/kg) = \frac{A_x \times V_t \times D \times 1000}{CF \times W} \quad \text{or} \quad \frac{(A_x - C) \times V_t \times D \times 1000}{S \times V_s}$$

Where:

A_x = peak area response for the analyte in the sample
CF = average calibration factor.
V_t = volume of total extract (1 mL).
W = weight of sample extracted (30 g).
D = dilution factor (if no dilution was made, D = 1)
1000 = factor converting kilograms to grams.
C = linear regression constant.
S = linear regression slope.

Concentrations determined by software -

$$\text{Concentration } (\mu g/kg) = \frac{R_x \times V_t \times D \times 1000}{W}$$

Where:

R_x = average concentration reported for sample, in µg (divide result by 1000 if concentration reported as mg).
V_t = volume of total extract (1 mL).
W = weight of sample extracted (30 g).
D = dilution factor (if no dilution was made, D = 1).
1000 = factor converting kilograms to grams

11.5.4 If an analyte is not present or present below the reporting limit (MDL), report the result as N.D. or 'non-detected'

11.6 PARSING DATA TO LIMS

All PCB analyses are manually entered into LIMS, based on pattern recognition and quantitation.

12.0 MAINTENANCE AND TROUBLESHOOTING

12.1 GENERAL

Glassware should be cleaned appropriately (see Section 4.0) to avoid sample contamination. Equipment should be kept clean and maintained to avoid sample contamination and assure proper operation. Manuals supplied by the manufacturers with the instrumentation typically have informational and troubleshooting sections.

12.2 TECHNICAL SUPPORT

Technical support is available from equipment manufacturers (for example, by telephone, fax, or e-mail). They can be a good resource when troubleshooting options have been exhausted. Technical support departments can readily supply part numbers.

12.3 ISOLATE THE PROBLEM

When troubleshooting the system for a chromatography or sensitivity problem, it is important to change only one thing at a time. A standard should be run after every change to see if any progress has been made.

12.4 INJECTION PORT

When maintenance of the injection port is indicated, for example, by a loss of resolution and/or peak response. The port should be cleaned with hexane, and all replaceable parts exchanged. The column may also be checked for slugs of grease, etc., and these portions of the column removed.

12.5 COLUMN INSTALLATION

Column re-installation is necessary whenever maintenance is performed to the injection or detection ports. A new column is required when the baseline is elevated or the chromatography is poor (*e.g.* poor peak shape and/or low response).

For column installation, first slide the appropriate nuts and ferrules over the ends of the column. Cut 15 cm off both ends of the column by scoring the coating with a sapphire scribe (or equivalent) and breaking the column at the score. Inspect the cut through a magnifying glass to ensure that there are no jagged edges. The proper lengths of the column (to the base of the ferrule nuts) to be inserted into the injection and detection ports are 2.7 mm and 72 mm, respectively. Mark the placement of the nut with typewriter correction fluid on the column as a point of reference. Tighten the nuts.

New columns must be conditioned before method validation. Leave the column disconnected from the detection port. Ramp the oven temperature up to just below its maximum, at 1°C/min, and hold for 4 hours.

12.6 COLUMN RINSING

The GC column may be rinsed with several column volumes of appropriate solvents (both polar and non-polar). Depending on the nature of the sample residues expected, the first rinse could be water, followed by methanol and acetone. Methylene chloride is a good final rinse, and in some cases, may be the only solvent required. The column should then be filled with methylene chloride and stored overnight to allow materials within the stationary phase to migrate into the solvent. The column is then flushed with fresh methylene chloride, drained, and dried at room temperature with a stream of ultrapure nitrogen gas.

13.0 REFERENCES

13.1 EPA Method 8000B, Gas Chromatography
13.2 EPA Method 8082 Polychlorinated Biphenyls (PCBs) by Capillary Column Gas Chromatography
13.3 Great Lakes Analytical Quality Assurance Program
13.4 Great Lakes Analytical Chemical Hygiene Plan.
13.5 Great Lakes Analytical SOP for Login Department.
13.6 Great Lakes Analytical SOP for Hazardous Sample Management.

14.0 DEFINITIONS

See References.

Figure 1.

Example Chromatogram for Aroclor 1016/1260 Mixture.

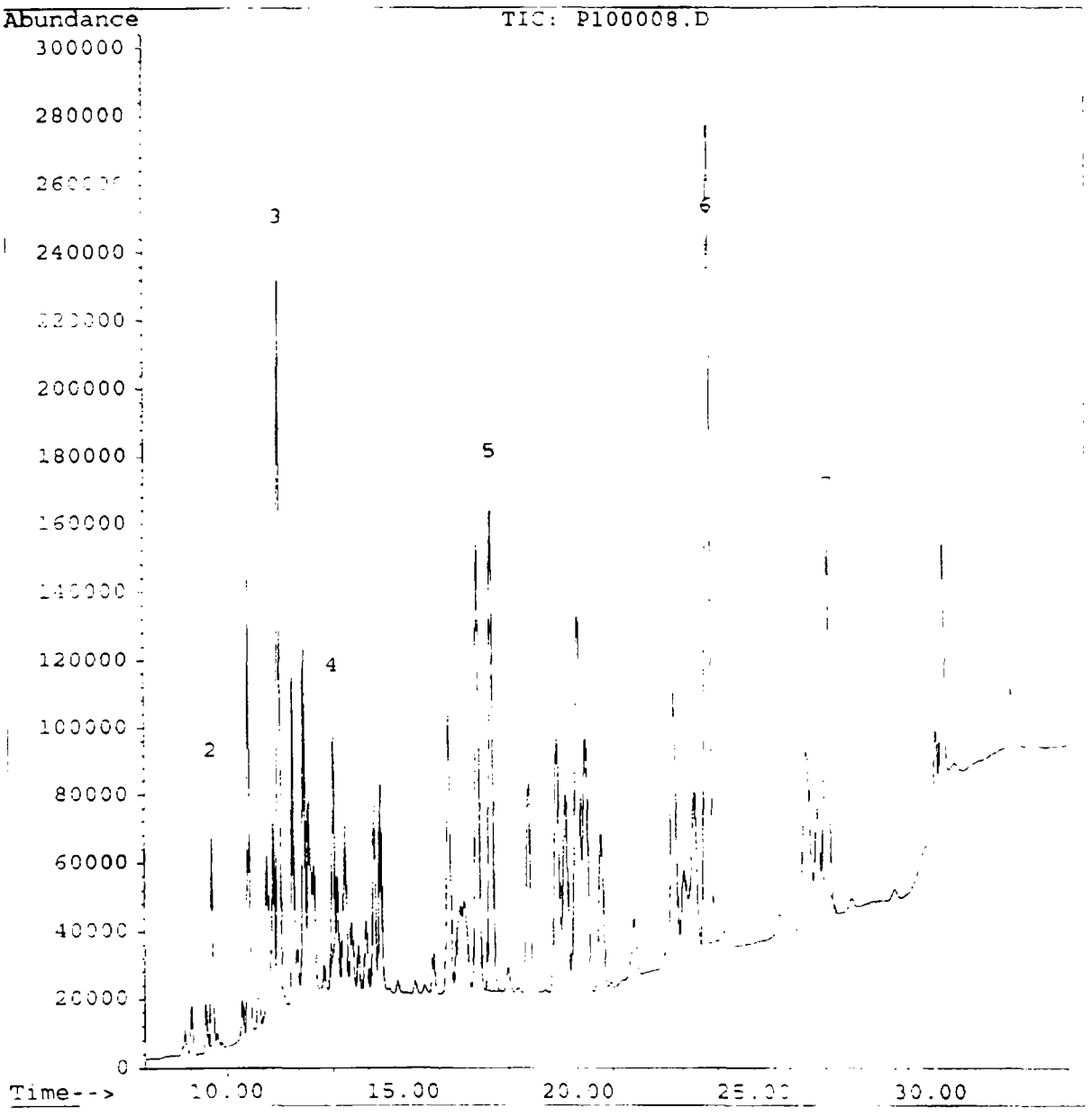
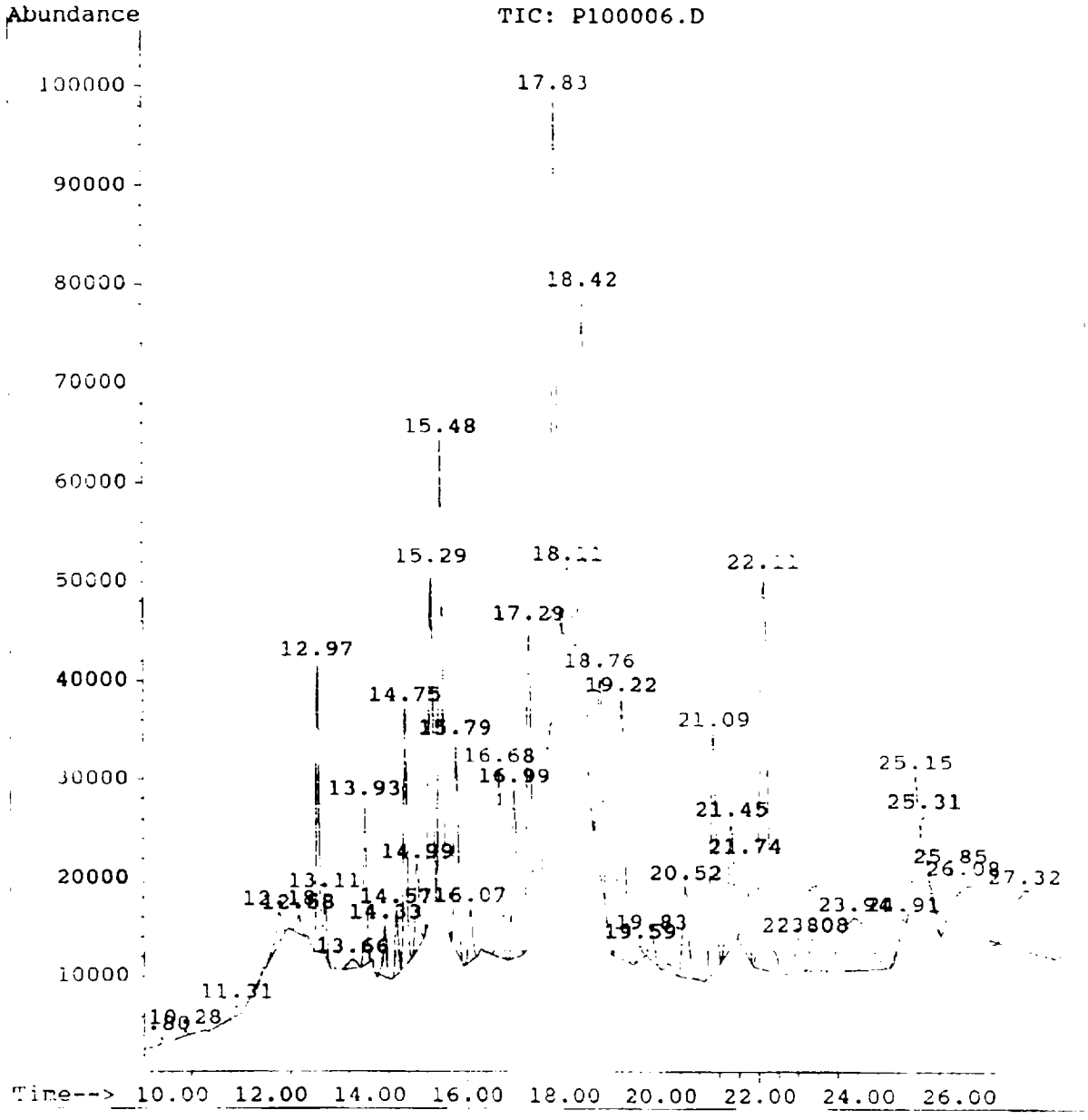


Figure 2.

Example Chromatogram for Aroclor 1254 Mixture.



GC Initial Calibration Checklist for PCBs (8082)

GC No.: _____ Date: _____

Review Item	YES	NO	Second Level Review
1 Does the curve consist of a calibration blank and the appropriate number of levels (at least 5)?			
2. Is the low standard near, but above, the MDL?			
3. Are response factors updated/curves drawn, and are RFs and %RSDs within QC limits (<20%)?			
4. Are the peak shapes well defined?			
5 Are retention time windows established and updated?			
6. Did the standard pass the resolution check criteria (concentration x opb. response ± 15%)?			

Analyst: _____ Date _____

Second-Level Review: _____ Date _____

Attachment 1

PCBs 8082 Daily Batch Checklist

GC No.: _____ Date: _____ Batch: _____

REVIEW ITEM	YES	NO	Second Level Review
A. Initial Calibration			
1. Has Prime and Blank been run?			
2. Are the 1016/1260 Check Standard %RSDs within QC limits?			
3. If another PCB other than 1016/1260 was detected, was the proper single-point calibration used?			
B. Sample Analysis (after all criteria have been met)			
1. Are all sample holding times met?			
2. Are all analytes out of calibration range diluted and reanalyzed?			
3. Are reported compounds within retention time windows?			
4. Are surrogate recoveries within limits?			
5. Has the Check Standard been run at the proper frequency?			
C. QC Samples			
1. Are the method blank concentrations less than the MDLs?			
2. Is the LCS recovery within QC limits?			
3. Are the MS/MSD recoveries/RPD within QC limits?			
D. Others			
1. Are all calculations checked at the minimum frequency?			
2. Did the analyst sign and date the appropriate printouts and report sheets?			
3. Red tag used for PCB concentrations greater than 50 ppm?			
4. Was a correction action filled out? CA #			

Comments on any "no" responses and/or re-analyzed samples

_____

_____

_____

_____

_____

_____

Analyst _____ Date _____

Second-Level Review _____ Date _____

Attachment 2

Standard Operating Procedure for the Determination of Volatile Organic Compounds by Purge-and-Trap and Gas Chromatography/Mass Spectrometry

GREAT LAKES ANALYTICAL

STANDARD OPERATING PROCEDURE

FOR

THE DETERMINATION OF VOLATILE ORGANIC COMPOUNDS

BY PURGE-AND-TRAP AND

GAS CHROMATOGRAPHY/MASS SPECTROMETRY

GLA 8260 BG

Revision 2.0

Approved By:

Department Manager _____ Date: 10 27 98

Quality Assurance Manager: _____ Date: 10/27/98

Laboratory Director: _____ Date: _____

1.0 APPLICABILITY

This procedure provides instructions for the analysis of samples for volatile organic compounds by a purge and trap extraction, followed by analysis with a gas chromatograph/mass spectrometer. This SOP is an interpretation of the SW-846 methods 8260B, 5030B, and 5035. It is to be used in conjunction with the analysts' in-laboratory training, the Great Lakes Analytical Chemical Hygiene Plan, and the Great Lakes Analytical Quality Assurance Program.

1.1 MATRICES

This method is applicable to water, soil, waste, and TCLP/SPLP matrices.

1.2 REGULATORY APPLICABILITY

40 CFR 121 (SW 846)

2.0 SUMMARY

This procedure describes the determination of volatile organic compounds by purge-and-trap, gas chromatography, and mass spectrometry. Helium is bubbled through a sample, purging out volatile components. These analytes are adsorbed onto a sorbent column (carbon trap). The trap is rapidly heated and backflushed with helium, desorbing the analytes onto a capillary column in a gas chromatograph. Once on the column, the analytes are separated by their interaction with the stationary phase of the column and the temperature program of the GC oven. The sample stream is reduced by a jet separator or a narrow bore restrictor column as it goes into the mass spectrometer. As analytes enter the detector, they are ionized by an ion source. Electrons fractionate the molecules, forming positive ions. Lenses focus the ion stream as it enters mass filtering quadrapoles. Varying AC and DC electronic signals on the quadrapoles permit ions with only certain mass to charge (*m/z*) ratios through the field. The filtered ion stream is then focused by another lens as it strikes the electron multiplier. The electron multiplier liberates neutralizing electrons that are proportional to ion abundance upon impact of the ion stream. The result is a total ion chromatogram as analytes are separated by the column with corresponding mass spectra in each peak. The peaks are identified by retention time and ion ratios. Each compound is assigned a primary characteristic ion. The area of this ion within its analytical peak is called an extracted ion current profile, or EICP of the characteristic ion. Quantitation is based upon generating response factors in a calibration study using EICP's for all compounds within the total ion chromatogram. Compounds which may be detected by this method are given in Appendix A.

3.0 SAFETY

3.1 GENERAL

This SOP does not address all safety issues associated with its use. A reference file of material safety data sheets (MSDS's) is available to all personnel, along with the Great Lakes Analytical Chemical Hygiene Plan.

The toxicity or carcinogenicity of each reagent used in this SOP has not been precisely determined; however, each chemical should be treated as a potential health hazard. Exposure to these chemicals should be reduced to the lowest possible level. Gloves and safety glasses are worn when handling solvents, chemicals, and reagents.

3.2 CHEMICAL HYGIENE PLAN

The Great Lakes Analytical Chemical Hygiene Plan (CHP) is designed to establish safe work procedures and minimize exposure to hazardous chemicals encountered in the laboratory. The CHP provides information to employees regarding potential hazards and training to minimize these hazards.

3.3 COMPRESSED GASES

All compressed gases, except air, can cause suffocation by displacing oxygen. Caution should be exercised when changing compressed gas cylinders. Analysts must wear safety glasses when changing cylinders or working with gas plumbing. All compressed gas cylinders must be secured at all times. A handtruck must be used to transport cylinders. The safety cap is to be in place at all times except when the cylinder is secured and a regulator is in place.

3.4 HAZARDOUS SAMPLES

All samples that are received by the laboratory have the possibility of containing hazardous pollutants. They should be treated with caution at all times. Gloves are worn when handling samples. Also see the Great Lakes Analytical SOP for Hazardous Sample Management.

3.5 STANDARDS

The standards used for calibrations and quality control are known pollutants, therefore caution should be taken when handling them. Standard preparation should take place in a hood or well-ventilated area. Gloves will be worn when handling standards. Benzene, carbon tetrachloride, 1,4-dichlorobenzene, 1,2-dichloroethane, hexachlorobutadiene, 1,1,2,2-tetrachloroethane, 1,1,2-trichloroethane, chloroform, 1,2-dibromoethane, tetrachloroethene, trichloroethene, and vinyl chloride are tentatively classified as known or suspected human or mammalian carcinogens, and should be handled accordingly.

4.0 INTERFERENCES

4.1 CONTAMINATION

Samples can become contaminated in the field or in transit. If trip and field blanks are analyzed with the sample group they can serve as a check for this type of contamination. A trip blank is a voa vial full of water that has accompanied the samples in transit. A field blank is a voa vial of reagent water that is poured through all the field equipment used in sampling. Contamination of samples can also occur during analysis from residue left by other samples in syringes, lines and glassware in the purge-and-trap, autosampler, column, or detector. A blank must be run through the analytical system every 12 hours to demonstrate that it is clean.

4.2 CARRYOVER

There are several ways residue, especially from a concentrated sample, can carryover into subsequent samples:

4.2.1 Trap carryover - All volatile components of a sample may not be sufficiently desorbed or baked off the trap, leaving residual hydrocarbons or specific analytes on the trap. These contaminants may come off the trap during the next run.

4.2.2 Glassware carryover - All volatile components may not be purged from the sample, leaving residual hydrocarbons or specific analytes in the glassware. These contaminants can be purged out with the next sample run in that position.

4.2.3 Line carryover - In a very concentrated sample, it is possible that the lines of the autosampler or purge-and-trap may become contaminated. This is evident when subsequent runs contain the same contaminant.

4.2.4 Column carryover - All of the hydrocarbons in a sample may not come off the column by the time the oven temperature program has finished. They elute as broad peaks in the next run.

If carryover is suspected for any reason, a blank should be run to verify a clean analytical system and any affected samples should be rerun. Individual autosampler positions should be baked out or have blanks run through them as necessary.

It is recommended that each purge-and-trap system have a "bake out" method that is performed before each analytical run. In this method, the line temperatures of the autosampler and the purge-and-trap are elevated and the autosampler positions are purged and baked without the addition of sample.

Syringe contamination and possible contamination from the extraction procedure are easily eliminated by rinsing syringes with water and spatulas with methanol between samples.

4.3 SAMPLE INTEGRITY

4.3.1 Samples submitted for volatiles analysis are kept at 4°C before analysis.

4.3.2 Water samples should be preserved with 1:1 hydrochloric acid in the field to pH<2 to kill any micro-organisms that may degrade the volatile aromatic compounds. Sample vials should be filled so that no headspace or air bubbles exist in the vial.

4.3.3 Soil samples are preserved based on the desired reporting limits. Low level soils are collected in containers that contain an aqueous solution of sodium bisulfate (1g of sodium bisulfate in 5ml water) as the preservative. High level soils are collected in containers which contain methanol as the preservative. Alternatively, soils may be collected in EnCore samplers, and sent to the lab for immediate transfering (within 48 hours of sampling) into vials with the appropriate preservative.

5.0 RECORD KEEPING

5.1 INSTRUMENT LOG

Each instrument has an Instrument Log. The instrument identification number and effective dates are written on the front cover. An instrument log is very helpful in tracking problems and is an important troubleshooting guide. Entries in this book include, but are not limited to:

- Installation of the instrument.
- Run parameters for the instrument, autosampler, and data system.
- Instrument and autosampler gas flows.
- All routine and unscheduled maintenance.

5.2 QUALITY CONTROL BOOK

A Quality Control Book is set up for each instrument. It has the instrument identification number on the outside cover. The contents of this book include

- Copy of the GLA Quality Assurance Program
- Copies of GLA SOP's and the source methods
- Copies of the calibration studies and internal standard control limits and the dates in use.
- Copy of the precision and accuracy study for the method.
- Copies of all method detection limit studies and dates in use.
- Copies of all retention time studies and dates in use.

- Check standard recovery tabulations and control limits.
- Spike and spike duplicate recovery tabulations and control limits.
- Surrogate standard recovery tabulations and control limits.
- Corrective action sheets.

5.3 RUN LOG

On the front cover of the Run Log notebook display:

- Instrument identification number.
- Run log number.
- Effective dates.

The following column headings are written at the top of each page

- Data file name
- Date
- Autosampler position.
- Client
- Full sample number.
- Amount of sample analyzed with units.
- Method number
- Results complete with units.
- Status of internal and surrogate standard recoveries.
- Comments.

Subsequent information for each sample and standard is then documented under the column headings. Additional documentation concerning standards includes:

- Quality control function (check standard, blank, matrix spike, etc.).
- Concentration.
- GLA code number.
- Recovery.

Each page is dated and signed Laboratory notebooks must be neat and legible. Mistakes are crossed out with a single line, initialed, and dated. Unused or partial pages are z'd out

5.4 SAMPLE SCHEDULE (LIMS)

Analysts keep track of sample throughput by using the LIMS (Laboratory Information Management System). The system is checked daily and all pertinent sample information is recorded, and a hard copy is generated. This information includes:

- Client name
- Sample numbers.
- Project name.
- Matrix.
- Hold time / turnaround time.

5.5 STANDARD PREPARATION LOG

When standards are received by the laboratory, the certificate of analysis is dated and placed in the Standards Preparation Certificate of Analysis binder. A log is kept of all the standards prepared for the volatiles methods Document in this book:

- Analyte Purpose (method. calibration, internal. etc).
- Supplier
- Lot number.
- Initial concentration of the stock solution.
- Volume diluted.

- Expiration date of stock standard - six months after the standard has been opened or the date set by manufacturer, whichever is first. Gas stock standards are good for one month after opened, or until the date set by the manufacturer, whichever is sooner.
- Final concentration.
- Volume prepared.
- Date prepared.
- Expiration date of working standard - three months after the standard has been made or when standard fails Quality Control criteria, whichever is first. Gas working standards expire after two weeks.
- GLA code for the final solution. The GLA code is a number and letter sequence used to track standard preparation within the department. It consists of the month number and successive letter of the alphabet starting with "A" at the beginning of each month.
- Initials

5.6 BALANCE LOG

A balance log is kept to check the accuracy of the scale used in soil sample extractions. Entries are made on any day the scale is utilized. Record:

- Date.
- Weight of the Class P check weight less the tared weight.
- Scale reading.
- Weight of second Class P check weight less the tared weight
- Scale reading
- Initial each entry.

Any problems and corrective action taken should also be recorded in this log.

6.0 QUALITY CONTROL

6.1 BFB TUNE CHECK

6.1.1 4-Bromofluorobenzene (BFB) must be analyzed at the start of every 12 hour sequence. 1µl (50ng) of the working tuning solution is directly injected onto the GCMS system.

6.1.2 Three scans (the peak apex scan and the scans immediately preceding and following the apex) are acquired and averaged. Background subtraction is required, and is accomplished by using a single scan prior to the elution of BFB. Other techniques can be used as long as the apex is always included and the other ions averaged are consecutive with the apex.

6.1.3 The key ions produced during the analysis of BFB and their respective ion abundance criteria are given below. This criteria must be met before any calibration standards, blanks, or samples can be analyzed.

Mass	m/z abundance criteria
50	15 to 40% of mass 95
75	30 to 60% of mass 95
95	base peak, 100% relative abundance
96	5 to 9% of mass 95
173	<2% of mass 174
174	>50% of mass 95
175	5 to 9% of mass 174
176	>95% but <101% of mass 174
177	5 to 9% of 176

6.2 CALIBRATION VERIFICATION (CV)

The CV validates the initial calibration curve and is used to gauge the daily operating condition of the instrument. The CV (at 50 µg/L) is analyzed every 12 hours, after the 12 hour tune, but before actual samples are analyzed.

6.2.1 The minimum relative response factors (RRF's) of system performance check compounds (SPCC's) must meet method requirements:

SPCC's	Min. RRF
Chloromethane	0.10
1,1-Dichloroethane	0.10
Bromoform	0.10
Chlorobenzene	0.30
1,1,2,2-Tetrachloroethane	0.30

$$RRF = \frac{EICP^{\bullet} \text{ of analyte}}{\text{concentration of analyte}} \cdot \frac{\text{concentration of internal standard}}{EICP^{\bullet} \text{ of internal standard}}$$

$^{\bullet}$ of the characteristic ion

Note: When determining the RF, the internal standard used in the calculation is the one which elutes closest to the analyte.

6.2.2 Calibration check compounds (CCC's) must also meet specific criteria. The CCC's are: 1,1-dichloroethene, chloroform, 1,2-dichloropropane, toluene, ethyl benzene, vinyl chloride. For CCCs which are calculated by average response factor, the percent difference (%D) between the RF of the CCC compound and the corresponding average RF from the calibration curve must be $\leq$ 20%. For CCCs calculated by linear regression, the percent drift must be $\leq$ 20%. If the CCCs are not part of the target analyte list, then all target compounds must meet the 20% criteria.

$$\%\ Drift = \frac{\text{known concentration - calculated concentration}}{\text{known concentration}} \times 100$$

The CCV can be used to check chromatography for peak shape. The check standard must fulfill the above criteria before samples can be analyzed.

6.3 METHOD BLANK

The method blank verifies that the analytical system is free from contamination.

6.3.1 The method blank is run every 12 hours, after the CV, but before samples are analyzed.

6.3.2 No contamination should be present in the blank above the reporting limit. If contamination is found, samples analyzed after the blank which contain the same contaminates must be reanalyzed to confirm the detects

6.3.3 The method blank may be the field blank sample submitted by a client for a particular project.

6.4 INTERNAL STANDARD

Internal standards are added to everything analyzed by this method. Recoveries are a factor in the concentration calculations of analytes. They also monitor the efficiency of the purge-and-trap extraction procedure.

6.4.1 The internal standards are pentafluorobenzene, 1,4-difluorobenzene, chlorobenzene-d_5, and 1,4-dichlorobenzene-d_4. The concentration of the internal standards is 50 ppb.

6.4.2 The retention times of the internal standards in the CVs must be within 30 seconds of retention times from the corresponding standard in the initial calibration.

6.4.3 The EICP areas of the characteristic ion of the internal standards in the CVs must be within 50% to 200% of those from the mid-point standard in the initial calibration.

6.4.4 When recoveries fall outside of the criteria, one sample from each effected project is re-analyzed to confirm a possible matrix effect. If the recoveries confirm, the data is reported from the original analysis and a corrective action form is filled out. If the recoveries of the internal standards fulfill criteria, the data from the re-analysis is reported.

6.5 SURROGATE STANDARDS

Surrogates are added to everything analyzed by this method. Surrogate standard recoveries are used to monitor the efficiency of the purge-and-trap extraction procedure.

6.5.1 The surrogate standards are dibromofluoromethane, 1,2-dichloroethene-d_4, toluene-d_8, and 4-bromofluorobenzene. The concentration of the surrogate standards is 50 µg/L.

6.5.2 The surrogate standard recoveries from 20 to 30 samples per matrix are tracked to determine the control limits. These limits are defined as the average recovery ± 3 times the standard deviation. Surrogate standard limits are kept in the QC binder and should be posted by the analyst for reference. Limits are determined annually.

6.5.3 When surrogate standard recoveries fall outside these limits, one sample from each effected project is re-analyzed to confirm a possible matrix effect. If the recoveries confirm, results are reported from the original analysis and a corrective action form is filled out. If the recoveries fulfill criteria, data from the re-analysis is reported.

6.6 MATRIX SPIKES

A set of matrix spike/matrix spike duplicates (MS/MSD) are analyzed regularly to check the effect of the sample matrix on the performance of the method.

6.6.1 An MS/MSD is analyzed per batch of 20 or less samples of the same matrix. Soil and water matrix spikes contain all of the analytes on the compound list at a concentration of 50µg/L and 50 µg/Kg, water and soil respectively. TCLP spikes contain all of the analytes on the compound list at a concentration of 100 µg/L, except for 2-butanone, which is at 500 µg/L.

6.6.2 Spike recoveries for all compounds per matrix are documented in tables for yearly tabulation of statistical limits. The spike recoveries must fall within the average spike recovery over a year per matrix for a particular compound ± 3 times the standard deviation. Limits are based in 20 sets of MS/MSDs. These limits should be posted by the analyst for reference.

6.7 LABORATORY CONTROL SPIKE (LCS)

The results of the LCS are used to verify the laboratory can perform the analysis in a clean matrix (ie. when MS/MSDs results indicate potential problems due to the sample matrix).

6.7.1 An LCS is analyzed with each 12 hour analytical batch. Reagent water (for water LCS) or clean sand (for soil LCS) is spiked at 50ppb with the same solution and at the same concentration as the MS/MSD.

6.7.2 Spike recoveries for all compounds per matrix are documented in tables for yearly tabulation of statistical limits. The spike recoveries must fall within the average spike recovery over a year per matrix for a particular compound ± 3 times the standard deviation. Limits are based in 20 sets of MS/MSDs. These limits should be posted by the analyst for reference.

6.8 CORRECTIVE ACTION

If a quality control measure fails, corrective action is taken and documented. Examples of when corrective sheets are filled out are:

- Check standard recovery fails for a particular compound that was present in the sample.
- Contamination was present in the blank and in the sample.
- Internal standard recovery is outside of 50-200% limits
- Surrogate recovery is outside of control limits.
- Matrix spike recoveries are outside of control limits.

6.8 CHECKLISTS

Checklists are designed to ensure that data being reported by the laboratory has met all of the daily quality control requirements. The analyst documents the status of all quality control requirements for an analytical batch by checking off and filling out Daily Batch Checklists prior to reporting results. If quality control criteria has failed, the analyst must document samples that were affected and whether or not corrective action was taken. (Please see attached checklists.)

7.0 SAMPLE MANAGEMENT

7.1 The procedure for sample management are detailed in the Great Lakes Analytical SOP for sample receipt into the laboratory.

7.2 HOLD TIME

7.2.1 Water samples preserved to a pH of less than 2 have a hold time of 14 days from the date sampled. Unpreserved water samples have a hold time of 7 days from the date sampled.

7.2.2 Soil samples received by the laboratory preserved with sodium bisulfate or methanol (see section 4.3) have a hold time of 14 days from the date sampled. Soil samples submitted to the lab in EnCore samplers, or in jars, must be preserved within 48 hours of sampling. Then, a holdtime of 14 days from the date of preservation is in effect.

7.2.3 Soil samples submitted for TCLP analysis must be zero headspace extracted within 14 days of sampling. An additional 14 day holdtime is in effect after the TCLP extraction has been performed.

7.2.4 If a sample is received or analyzed past the holdtime, the client is immediately informed of the problem, and the report is qualified.

7.3 SAMPLE SCHEDULE

Analysts keep track of sample throughput by using the Laboratory Information Management System (LIMS). The system is checked daily and a hard copy generated. Samples for method 8260 are queued under "VOMS". The information includes:

- Client name.
- Sample numbers.
- Project name.
- Matrix.
- Hold time and turnaround time.

7.4 DISPOSAL

The analyst disposes of extracted samples one week after the date of analysis. Methanol and remaining fluid in the purge tubes is placed in the solvent drum. The login department maintains the other volatiles refrigerators. TCLP/SPLP extracts are disposed of one week after analysis. The extract is poured into the acid waste drum.

7.5 HAZARDOUS SAMPLES

If upon sample analysis analytes with concentrations above "Red Tag Limits" are found, the login department is notified by filling out a red tag sheet, and red tape is placed on the sample container. (See the GLA SOP for Hazardous Sample Management.)

RED TAG LIMITS

Compound	mg/kg	mg/L
Benzene	8	0.4
Carbon tetrachloride	8	0.4
Chlorobenzene	1600	80
Chloroform	96	4.8
1,2-Dichloroethane	8	0.4
1,1-Dichloroethene	11	0.56
Methyl ethyl ketone	3200	160
Tetrachloroethene	11	0.56
Trichloroethene	8	0.4
Vinyl chloride	3.2	0.16

8.0 METHOD VALIDATION

8.1 INITIAL CALIBRATION STUDY

An initial calibration study determines the average response factors for the target and surrogate analytes that in turn are used to quantitate the concentration of these compounds in a sample. An internal standard calibration technique is employed in which the same concentration of internal standard is added to a series of freshly prepared calibration standards which encompass the linear range of the detector. The initial calibration must be developed before samples, blanks, and QC samples can be analyzed.

8.1.1 A minimum of five calibration levels are prepared and analyzed. Typically, these levels range from 5 ppb to 400 ppb. All target analytes, including surrogates, must be included in the each calibration level. Internal standards (at 50 ppb) are also added to each calibration level.

8.1.2 The RRFs are calculated (see 6.2.1) for each target analyte and surrogate in each calibration level. The average RRF is then calculated for all analytes, using all of the levels in the calibration study.

8.1.3 The average RRF's for the SPCCs must meet the minimum RRF requirements specified in section 6.2.1.

8.1.4 The percent relative standard deviation (%RSD) is calculated for all the analytes:

$$\%RSD = \frac{\text{standard deviation}}{\text{average RF}} \times 100$$

8.1.5 The %RSD for the CCCs (section 6.2.2) must be ≤ 30%.

8.1.6 If the %RSD is ≤ 15% for all included analytes, then the calibration is considered linear, and the average RRF is used for quantitating samples, blanks, and QC. However, if the %RSD exceeds 15%, a least squares linear regression curve must be created for each analyte above the 15%.

$y = mx + b$

where y = EICP area for the analyte
m = Slope of the curve
x = Concentration of the calibration standard
b = The y intercept of the curve

Note: The correlation coefficient generated by the regression must be ≥ 0.99 in order for it to be used for quantitation purposes.

8.1.7 If any of the above criteria is not met for the calibration, corrective action is performed, and another calibration study is analyzed.

8.2 DETECTION LIMIT STUDY

This study is performed in accordance with the GLA Quality Assurance Program. This study provides the analyst with the method detection limit (MDL) for the instrument and analytes. The MDL is defined as the minimum concentration of the analyte that can be measured and reported with 99% confidence. The MDL is equal to the standard deviation of the recoveries of seven aliquots multiplied by the analysts t value appropriate for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom. The analysts' t value appropriate for 7 aliquots is 3.143. The calculated MDL must be between 100% and 10% of the concentration of the MDL standard in order to be valid. An MDL study is done yearly per matrix.

- Run 7 replicate low level standards (at or below lowest calibration level standard).
- MDL = standard deviation × 3.143.
- The calculated MDL must be less than reporting limit.

8.3 ACCURACY AND PRECISION STUDY

To establish the ability to generate acceptable accuracy and precision, the analyst must perform the following operation:

- Run 4 replicate standards at 50 µg/L.
- Recoveries of all compounds must be between 80-120%.
- The relative standard deviation must be less than 20%.

The study is performed by each analyst in charge of a new method, or when major maintenance is performed (changing a column, changing oven parameters).

9.0 EQUIPMENT

9.1 System 1 -

Purge-and-trap system:

- Tekmar LSC 2000 sample concentrator.

- Tekmar Archon autosampler.
- Supelco VOCARB 3000 trap - 10 cm Carbopack B, 6 cm Carboxen 1001.

Operating parameters:
- Purge pressure: 20 psi.
- Purge flow: 40 mL/min.
- Purge time: 11 min.
- Desorb time: 4 min. at 240°C
- Bake: 10 min. at 260°C

Hewlett Packard 5890 Gas Chromatograph equipped with a Restek RTX-502.2 0.53 mm ID X 60 m column, Jet Separator interface and Hewlett Packard 5971 MSD. (GC/MS-1. Installed 7/91.)
Oven parameters.
- Mass spectrometer interface (Detector B) temperature: 250°C.
- Jet separator temperature (Detector A): 200°C.
- Injector temperature: 250°C.
- Temperature program: 36°C for 10 minutes increase 8°C/min. to 210°C, hold for 1 min.

Linear velocity of helium at 150°C: 59 cm/sec.
Column head pressure at 35°C: 6 psi.
Hewlett Packard Chemstation and Enviroquant Data Management System.

9 2 System 2 (for low level soils)-

Purge-and-trap system:
- Tekmar LSC 3000 sample concentrator.
- Tekmar 2016 Purge and Trap Autosampler.
- Supelco VOCARB 3000 trap - 10 cm Carbopack B, 6 cm Carboxen 1001.

Operating parameters:
- Purge pressure: 20 psi.
- Purge flow: 40 mL/min.
- Purge time: 11 min.
- Desorb time: 4 min. at 240°C
- Bake : 10 min. at 260°C

Hewlett Packard 5890 Gas Chromatograph equipped with a J&W DB 624 0.53 mm ID X 75 m column, narrow-bore restrictor column interface, and Hewlett Packard 5972 MSD. (GC/MS-3, installed 10/94.)
Oven parameters.
- Mass spectrometer interface (Detector B) temperature: 250°C.
- Injector temperature: 250°C.
- Temperature program: 40°C for 10 minutes increase 8°C/min to 220°C hold for 3 min.

Linear velocity of helium at 110°C: 37 cm/sec.
Column head pressure at 35°C: 8 psi
Hewlett Packard Chemstation and Enviroquant Data Management System

Specific instrument parameters can be found in the instrument maintenance log.

10.0 STANDARDS AND REAGENTS

10.1 STANDARD SOURCES

Standards are ordered from EPA or A2LA Certified companies. These companies include Accustandard, Restek, Supelco, and Ultra Scientific.

10.2 STANDARD DILUTIONS

Standards are volatile so special care should be taken to preserve their integrity. Stock and working standards are kept in a freezer between -10 and -20°C when not in use.

A useful equation for standard preparation is:

$$C_1V_1 = C_2V_2$$

Where:
C_1 is the initial concentration of the stock standard
C_2 is the desired concentration of the working standard.
V_2 is the volume of working standard to be prepared.
V_1 is the volume of stock standard to be diluted.

10.3 STOCK STANDARD

Transfer stock standard to a vial and seal with Teflon-lined cap. Label this vial with:
Analyte description
Manufacturer.
Lot number.
Concentration.
Date opened.
Expiration date.

Store in a freezer. The stock standard expires six months after it is opened or the expiration date set by the manufacturer, whichever is first. Opening of the standard is documented in the Volatile Standard Log.

10.4 WORKING STANDARD

Standards are diluted in methanol.

- Fill a volumetric flask about three quarters of the way full with methanol.
- Add desired amount of stock standard.
- Fill volumetric flask to meniscus.
- Cap and invert three times.
- Transfer to vial with "mini-nert" cap.
- Label vial with:
  - Analyte description.
  - Concentration of standard.
  - Date made.
  - Purpose.
  - Initials.
  - Expiration date.
  - GLA code.

The working standard expires three months after it is opened or when the standard fails Quality Control Criteria, whichever is first. Preparation is documented in the Volatile Standard Log.

10.5 REAGENTS

10.5.1 Methanol - Purge-and-trap grade methanol is used for extractions and standard preparation.
10.5.2 Reagent water – Bottled drinking water is boiled for three minutes and then purge with nitrogen before use in analyses
10.5.3 Gases - Ultra-high purity grade helium.

11.0 PROCEDURE

11.1 Before samples can be prepared for loading onto the instrument, all utensils must be cleaned. Syringes used for fortifying samples are rinsed several times with purge and trap grade methanol. 5ml syringes are rinsed several times with reagent grade methanol and twice with reagent water. Purge vessels are also rinsed several times with reagent grade methanol, and twice with reagent water.

11.2 Before anything can be loaded and analyzed, the purge and trap autosampler must be cleaned This involves flushing the sample valves and sparger needles with several mls of a 1:1 water/methanol mix. A plastic 25ml syringe is twisted onto the sample valve, the valve is opened, and several mls of the mix is injected through the valve and collected at the end of the sparger needle with a 500 ml plastic beaker. The sparger needle is wiped clean with a kimwipe. This process is repeated for each autosampler port.

11.3 If highly concentrated samples (eg. exceed the calibration range) have been analyzed on the instrument (on column concentrations > 400 ppb), a bake-out procedure is required. This involves purging each port for 2 minutes and heating each sample line to 180 °C. Consult instrument maintenance procedures for complete details.

11.4 A typical analytical run would be as follows:

BFB Tune
Calibration Std #1
Calibration Std #2
Calibration Std #3
Calibration Std #4
Calibration Std #5
} Analyze calibration curve as needed
CV
Method Blank
QC Check Sample
Sample Analysis (# of samples dependent on 12 hour clock)
MS (per 20 samples or less by matrix)
MSD (per 20 samples or less by matrix)

11.5 All of the following procedures and the order of analysis must be documented in the Volatiles Run Logbook.

11.6 Before analyzing calibration standards, CVs, blanks, QC, and samples, a BFB tune is analyzed by injecting the appropriate amount of the working BFB tune solution (50 ng on-column). All the criteria in Section 6.1.3 must be met before proceeding with the typical run outlined above

11.7 After an acceptable BFB tune has been analyzed, an initial calibration is prepared and analyzed. A minimum of five calibration standards are prepared in 5 ml of reagent water (in 5ml sodium bisulfate preservative solution for low level soils using the Archon autosampler), and analyzed from low (5ppb) to high (400ppb) concentration. All the criteria in Section 8.1 must be met before samples can be analyzed

11.8 Once an initial calibration is established, a CV is prepared (@50ppb) in 5 ml of reagent water (in 5ml sodium bisulfate preservative solution for low level soils using the Archon autosampler) and analyzed. All the criteria in Section 6.2 must be met before samples can be analyzed.

11.9 Next, a method blank is prepared in 5 ml reagent water (5ml sodium bisulfate preservative solution for Archon autosampler) by fortifying the water with internal standard and surrogate only (@ 50ppb). The analytical results must fulfill Section 6.3 before samples can be analyzed.

11.10 Finally, an LCS is prepared (@50ppb) in 5 ml reagent water (5ml sodium bisulfate preservative solution with ~ 5.0g clean sand for Archon autosampler), or 5g of clean sand (med/high level soils), and analyzed. The recovery limits described in Section 6.7 should be fulfilled.

11.11 Once 11.6 through 11.10 have been completed, samples can be analyzed.

11.12 Water Sample Analysis

11.12.1 All samples are removed from the volatiles storage refrigerator and allowed to reach room temperature.

11.12.2 Water samples are prepared in 5ml syringes. The plunger is removed from the syringe and the syringe barrel is filled with the sample.

11.12.3 The plunger is placed into the barrel, and the volume is adjusted to 5ml, taking care of eliminating any air bubbles in the syringe

11.12.4 The appropriate amount of internal standard/surrogate is added (50ppb), and the sample is loaded onto the instrument.

11.12.5 As explained in section 6.6, a set of MS/MSDs must be analyzed at a regular interval. A pair of samples is prepared as described above except an appropriate amount of spiking solution is also added to each synnge.

11.12.6 All compounds must fall within the established calibration range. Dilutions of water samples are prepared in 5ml syringes. Dilutions should be made to get the majority of the target compounds within the upper half of the calibration. Aliquots of the sample are added to reagent water to obtain a final volume of 5ml. For high level water samples, volumetric flasks are used to make serial dilutions before diluting to a final volume of 5ml.

11.12.7 After a water sample has been loaded, the pH of the sample is taken by dipping a pH strip into the opened sample vial. The pH is recorded in the Volatiles Run Logbook.

11.13 TCLP/SPLP Sample Analysis

11.13.1 After the samples are leached by the zero headspace technique, samples are given to the Volatiles group for analysis.

11.13.2 Leached samples are prepared in 5ml syringes. The plunger is removed from the syringe and the syringe barrel is filled with reagent water.

11.13.3 The plunger is placed into the barrel, and the volume is adjusted to 4.75ml, taking care of eliminating any air bubbles in the syringe.

11.13.4 Then, 250µl of the leached sample is added to the syringe.

11.13.5 The appropriate amount of internal standard/surrogate is added (50ppb), and the sample is loaded onto the instrument.

11.13.6 As explained in section 6.6, a set of MS/MSDs must be analyzed at a regular interval. A pair of samples is prepared as described above except an appropriate amount of spiking solution is also added to each syringe

11.13.7 All compounds must fall within the established calibration range. Dilutions of water samples are prepared in 5ml syringes. Dilutions should be made to get the majority of the target compounds within the upper half of the calibration. Aliquots of the sample are added to reagent water to obtain a final volume of 5ml. For high level water

samples, volumetric flasks are used to make serial dilutions before diluting to a final volume of 5ml.

11.14 Low Level Soil Analysis

11.14.1 This procedure is used for samples preserved with sodium bisulfate. Estimated concentrations for this procedure are projected to be < 200 µg/Kg.

11.14.2 The exact amount of soil in each vial is determined and documented in the Volatiles Extraction Logbook. The weight is determined by subtracting the weight of the vial containing the preservative and stir bar from the vial containing the preservative, stir bar, and soil.

11.14.3 All samples are removed from the volatiles storage refrigerator, and allowed to reach room temperature

11.14.4 The sample vials, containing ~5.0g of soil, 5ml of the sodium bisulfate preservation solution, and a stir bar, are gently shaken to insure free flowing of the sample for stirring. Vials are then placed into the Archon autosampler.

11.14.5 The autosampler then automatically adds 10ml of reagent water, and 1µl of the internal standard/surrogate solution (final conc.=50ppb).

11.14.6 The contents of the vials are preheated to 40°C, and then stirred and purged for 11 minutes The purge effluent is then transferred onto the sorbent trap of the concentrator, and in turn, desorbed into the instrument for analysis.

11.14.7 As explained in section 6.6, a set of MS/MSDs must be analyzed at a regular interval. A pair of samples is prepared as described above except an appropriate amount of spiking solution is manually added through the vial septum using a gastight syringe.

11.14.8 If concentrations of target analytes exceed the calibration range, an alternative analytical procedure is required (high level soil analysis).

11.15 Direct Soil Purge Analysis

11.15.1 Unpreserved soil samples may be directly purged following "old" methodology. Client approval is required to perform this analysis.

11.15.2 All samples are removed from the volatiles storage refrigerator, and allowed to reach room temperature.

11.15.3 First, 5g (±0.05g) of soil is weighed into a purge vessel using a top loading balance and the weight is recorded in the Run Log. The purge vessel is then loaded onto the instrument.

11.15.4 Next, 5mls of reagent water is prepared following the same procedure as for a method blank (Section 11.9). This is added to the purge vessel on the instrument that contains the soil sample.

11.15.5 As explained in section 6.6, a set of MS/MSDs must be analyzed at a regular interval. A pair of samples is prepared as described above except an appropriate amount of spiking solution is also added to the 5ml of water added.

11.15.6 All sample results must fall within the established calibration range. Dilutions should be made to get the majority of the target compounds within the upper half of the calibration. Smaller aliquots of the sample are weighed into the purge vessel.

However, no less than 0.5g of sample is used for analysis. For high level soil samples, the med./high level soil preparation procedure is used for diluting.

11.16 High Level Soil Analysis

11.16.1 This procedure is used for methanol preserved soil samples, or for unpreserved soils and waste samples that are expected to have concentrations of target compounds in excess of 200µg/Kg.

11.16.2 All samples are removed from the volatiles storage refrigerator, and allowed to reach room temperature.

11.16.3 For methanol preserved samples, the exact amount of soil in each vial is determined and documented in the Volatiles Extraction Logbook. The weight is determined by subtracting the weight of the vial containing the preservative from the vial containing the preservative and soil. The standard methanol to soil for preserved samples is 2:1; however, 1:1 ratio is also an acceptable ratio. Moreover, a definite ratio is needed in order to determine the dilution factor for the extraction. Proceed to 11.16.5.

11.16.4 For unpreserved soils, or waste samples, 10.0g (+/- 0.05g) of sample is weighed into a clean extraction vial. 5ml of methanol is added to the vial. This preparation is documented in the Extraction Logbook. Other sample and methanol amounts can be used; however, the ratio chosen must result in a total submerging of the sample by the methanol.

11.16.5 Before samples are extracted, the appropriate amount of surrogate is added to each vial, so that the resulting on-column concentration is 50µg/Kg. Since this addition could effect the ratio of methanol to soil, good documentation is needed. An addition of $\leq$100µl of the surrogate solution is negligible.

11.16.6 Shake the sample vials for two minutes, and allow to settle.

11.16.7 While the sample is settling, fill a 5ml syringe to 4.9ml with reagent water.

11.16.8 Once the sample has settled, remove a 100µl aliquot of the methanol extract, and add it to the 5ml syringe prepared in 11.16.7. Then, add the appropriate amount of internal standard (50µg/Kg).

11.16.9 As explained in section 6.6, a set of MS/MSDs must be analyzed at a regular interval. A pair of samples is prepared as described above except an appropriate amount of spiking solution is also added to the vials before extraction, keeping in mind the methanol/sample ratio.

11.16.10 All sample results must fall within the established calibration range. Dilutions should be made to get the majority of the target compounds within the upper half of the calibration. Samples are diluted further by varying the amount of extract added to the purge water. The amount of extract added must be $\geq$ 10µl and $\leq$ 100µl. For larger dilutions, serial dilutions of the extract are performed using volumetric flasks.

11.17 General Analysis Notes

11.17.1 Each analytical batch must be completed within a 12 hour time frame. Any analysis performed outside the 12 hour clock must be reanalyzed. The twelve hour clock starts at the time of the BFB tune.

11.17.2 All compounds must fall within the established calibration range, unless the client allows sample results to exceed the calibration range. Reported results which exceed the calibration range are flagged as estimated.

11.17.3 If exceedance of the calibration range is allowed, reanalysis is still required if the exceeding result is below the requested reporting limit.

11.17.4 If a sample is analyzed immediately following a highly concentrated sample, reanalysis of the sample should be considered.

11.17.5 If a highly concentrated sample (>400 ppb for any target compound) is analyzed on a port, instrument blanks must be analyzed in that port until analytical results show no detection above the reporting limit. An instrument blank is prepared the same as a method blank.

11.18 Qualitative Analysis

11.18.1 Qualitative identification of compounds is based on relative retention time (RRT) and on comparison of the sample mass spectrum, after background correction, with characteristic ions in a reference mass spectrum. Appendix A lists the characteristic ions for all the target compounds.

11.18.2 The RRT of the suspected constituent in the sample must be within ± 0.06 RRT units of the RRT of the standard compound.

11.18.3 The intensities of the characteristic ions of a compound should maximize in the same scan, or within one scan of each other. This is determined automatically with the data systems target compound search routine.

11.18.4 The relative intensities of the characteristic ions should agree within 30% of the relative intensities of these ions in the reference spectrum (ex. For an ion abundance of 50% in the reference spectrum, the corresponding abundance in the sample spectrum can range between 20% and 80%).

11.18.5 For those isomer compounds that produce very similar mass spectra, the retention time should be used to identify the individual isomers.

11.18.6 If a compound cannot be verified by the above criteria, but in the technical judgement of the analyst, the identification is correct then the compound shall be reported.

11.19 Quantitative Analysis

11.19.1 After a compound has been qualitatively identified following Section 11.18, the concentration of a target compound can be calculated based on the EICP area of the compound. Integration of EICP of the characteristic ion is performed automatically by the data system.

11.19.2 Manual integrations done specifically to meet method or contract quality control requirements are not permitted. There are situations when manual integration may be necessary, such as complex samples where partial coelution of peaks occur, or when the baseline has not been assigned adequately by the data system. In the instances, the trained analyst shall use their best technical judgement in the integration of the chromatogram.

11.19.3 The internal standard technique is used for quantitation (see Section 8.1). If the RSD from the calibration for a compound is ≤15 %, then the AvgRRF maybe used in the

calculation of the concentration. If the RSD from the calibration for a compound is >15%, then the linear regression is used to calculate the concentration.

12.0 CALCULATIONS

12.1 Water Samples (using AvgRRF)

$$\text{Concentration } (\mu g/L) = \frac{(A_x)\,(I_s)\,(DF)}{(A_{is})\,(\text{AvgRRF})\,(V_o)}$$

where,

A_x = Area of the characteristic ion of the compound
A_{is} = Area of the characteristic ion of the internal standard
I_s = IS amount in nanograms (ng)
AvgRRF =Average relative response factor from the calibration
V_o = Final volume of water purged in ml's (5ml)
DF =Dilution factor. The dilution factor for analysis of water samples for volatiles by this method is defined as the ration of the number of milliliters (mL) of water purged (i e. Vo above) to the number of mL of the original water sample used for purging. For example, for TCLP samples, 0.25ml of sample is diluted to 5.0 mL with reagent water and purged — DF=5.0mL/0.25mL = 20 If no dilution is performed, Df = 1.0.

12 2 Low Level Soils (Using AvgRRF)

$$\text{Concentration } (\mu g/L) = \frac{(A_x)\,(I_s)}{(A_{is})\,(\text{AvgRRF})\,(V_o)}$$

where,

A_x = Area of the characteristic ion of the compound
A_{is} = Area of the characteristic ion of the internal standard
I_s = IS amount in nanograms (ng)
AvgRRF =Average relative response factor from the calibration
V_o = Final weight of soil purged in grams

12.3 Soil/Sediment/Waste Samples (using AvgRRF)

$$\text{Concentration } (\mu g/Kg) = \frac{(A_x)\,(I_s)\,(V_t)}{(A_{is})\,(\text{AvgRRF})\,(V_i)\,(W_s)\,(D)}$$

where.

A_x , A_{is} , I_s and AvgRRF are the same as for the water calculation above
V_t = For Med/High level samples: Volume of total extract (µl)
V = For Med/High level samples: Volume of extract added for purging (µl)
W_s= Weight of sample extracted or purged (g)
D= % dry weight. where D= (100- %moisture)/100

12.4 Sample Quantitation by Linear Regresion: Samples which require quantitation from a linear regression calibration curve will follow the following general equation:

$$C = (m\,(A) + b) \times DF$$

where,

C= Concentration of the compound

m = Slope of the calibration curve
A = Ratio of the sample EICP area to the internal standard EICP area
b = Intercept of the calibration curve (based on order of regression used)
DF = Dilution factor (based on 5ml, 25ml, or 5g of sample purged)

12.5 Surrogate Percent Recovery

$$\% \text{ Recovery} = \frac{\text{concentration found}}{\text{concentration spiked}} \times 100$$

12.6 Matrix Spike Recovery

$$\% \text{ Recovery} = \frac{SSR - SR}{SA} \times 100$$

where,

SSR = spiked sample result
SR = sample result
SA = spike added

12.7 Relative Percent Difference (RPD)

$$RPD = \frac{|(MSR - MSDR)|}{(1/2)(MSR+MSDR)} \times 100\%$$

where.

MSR = matrix spike recovery
MSDR = matrix spike duplicate recover

13.0 REPORTING NOTES

13.1 Data is reported in µg/kg or µg/L. This is equal to parts per billion, or ppb

$$\frac{\mu g}{kg} = \frac{\mu g}{kg} \times \frac{1000\ ng/\mu g}{1000\ g/kg} = \frac{ng}{g}$$

$$\frac{\mu g}{L} = \frac{\mu g}{L} \times \frac{1000\ ng/\mu g}{1000\ mL/L} = \frac{ng}{mL}$$

13.2 If an analyte is present below the reporting limit or is not present at all, it reported as N.D. or "not detected".

13.3 If a sample is analyzed with dilution, a dilution factor needs to be applied to the reporting limit. Reporting limits are based on full strength sample aliquots of 5.0g for soils, 5.0ml for waters, and 250µl for TCLP extracts.

$$\textit{Dilution factor (DF)} = \frac{\textit{full strength}}{\textit{amount analyzed}}$$

Raised reporting limit = reporting limit x DF

14.0 LIBRARY SEARCH

14.1 Tenatively Identified Compounds (TICs): To identify compounds which are not part of the targeted and calibrated list, a library search is performed on the mass spectra to determine tenative identification.

14.2 Relative intensities of major ions in the reference spectrum (ions >10% of the most abundant ion) should be present in the sample spectrum.

14.3 The relative intensities of the major ions should agree within ±20%(ex. For an ion abundance of 50% in the standard spectrum, the corresponding abundance in the sample spectrum can range between 30% and 70%).

14.4 Molecular ions present in the reference spectrum should be present in the sample spectrum.

14 5 Ions present in the sample spectrum but not in the reference spectrum are reviewed for possible background contamination or coelution of another compound.

14 6 Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible background subtraction by the data system

14.7 If in the technical judgement of the mass spectral interpretation specialist, no valid tentative identification can be made. the compound shall be reported as unknown. Additional classification shall be made if possible (i.e. Unknown hydrocarbon).

The 10 largest non-target peaks on the chromatogram are quantitated against the closest eluting internal standard. The RF for each unknown compound is assumed to be one.

15.0 INSTRUMENT MAINTENANCE LOG

It is very important to maintain an accurate and detailed instrument maintenance log. Document all problems and attempts at correcting them as well as results. This information is invaluable when the problem recurs and a clear solution is laid out. Documentation of routine maintenance such as changing tanks and cleaning the detector can also provide insight into a subsequent problem.

16.0 TROUBLESHOOTING

When troubleshooting the system for a chromatography or sensitivity problems it is important to isolate the problem. Only change one thing at a time. A standard should be run after every change to see if any progress has been made. The instrument maintenance log should have all run parameters documented. Check these parameters to see if they have changed.

16 1 Direct Inject: A direct injection bypasses the purge-and-trap system. If the direct injection looks bad. the problem is with the gas chromatograph or the detector. If the direct inject looks good, then the problem probably is with the purge-and-trap system.

16.2 Checking flows: Attach flow meter to vent on the sample concentrator. Step to purge. Measure flow in ml/min. by using timer on GC.

16 3 Checking for leaks: Use the Gowmac leak detector at all unions in the injection port, in the detector, at the regulators on the GC or use methanol to see if it bubbles. To leak check the purge-and-trap, cap off the vent on the sample concentrator. Step the unit to purge. The sparge vessel should stop bubbling at about 7 minutes. If the instrument stops bubbling before 6 minutes there is a leak in gas lines before the sparge vessel. If the instrument continues to bubble past 8 minutes there is a leak in the gas lines after the sparge vessel. The MSD can be set up to look for the mass of methanol. Enter the mass of methanol (31) into the scan parameters and squirt methanol around any unions. If there is leak the methanol mass peak will get larger as the methanol reaches the detector.

16.4 Column installation: Column re-installation is necessary whenever maintenance is done to the injection or detection ports. A new column is necessary when there is an elevated baseline or the chromatography is bad. To install a column, slide the appropriate nuts and ferrules over the ends of the column. Cut 15 cm off both ends of the column by scoring the coating with a sapphire scribe (or equivalent) and breaking the column at the score. Inspect the cut through a magnifying glass to insure that there are no jagged edges. Consult the instrument manual for the proper length of the column to be inserted into the injection or detection ports. Mark the placement of the nut with typewriter correction fluid on the column as a point of reference. If the column is new, it must be conditioned before it is ready for method validation. Leave the column disconnected from the detection port. Ramp the oven temperature up at 1°C/min. to just below its maximum and hold for 4 hours.

16.5 Other sources of problems

16.5.1 Trap - Indications of a bad trap are: benzene in the blank, decreased internal area, back-pressure in the autosampler, decreased carbon tetrachloride response.

16.5.2 Standards - Bad standards are easily detected by analyzing them on multiple instruments.

16.5.3 Glassware - Indication of glassware or autosampler position problems include poor check standard or spike recoveries repeatedly in one position, poor surrogate and internal standard recoveries always in the same position.

16.5.4 Injection port - Due to the direct injections of BFB, it is often necessary to change the septa in the injection port so that there is not a leak.

16.5.5 Dirty detector - Indications of a dirty detector include: BFB will not pass specification; Low high mass abundance High background; High EM voltage

17.0 REFERENCES

17.1 SW-846 Method 5030B: Purge-and-Trap for Aqueous Samples.
17.2 SW-846 Method 5035: Closed-System Purge-and-Trap and Extraction Volatile Organics in Soil and Waste Samples.
17.3 SW-846 Method 8260B: Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry.
17.4 Great Lakes Analytical Quality Assurance Program Manual.
17.5 Great Lakes Analytical Chemical Hygiene Plan
17.6 Great Lakes Analytical SOP for Login Department.
17.7 Great Lakes Analytical SOP for Hazardous Sample Management.

APPENDIX A.

DETECTABLE COMPOUNDS.

	Primary Characteristic Ion		Primary Characteristic Ion
Acetone[a,b]	58	1,3-Dichloropropane	76
Acrolein	56	2,2-Dichloropropane	77
Acrylonitrile	53	1,1-Dichloropropene	75
Benzene[a,b]	78	cis-1,3-Dichloropropene[a]	75
Bromobenzene	156	trans-1,3-Dichloropropene[a]	75
Bromochloromethane	128	Diisopropyl ether	45
Bromodichloromethane[a]	83	Ethyl benzene[a,b]	91
Bromoform[a]	173	2-Hexanone[a]	43
Bromomethane[a]	94	Hexachlorobutadiene	225
2-Butanone (MEK)[a,b]	72	Isopropyl benzene	105
n-Butylbenzene	91	p-Isopropyltoluene	119
sec-Butylbenzene	105	4-Methyl-2-pentanone (MIBK)[a,b]	100
tert-Butylbenzene	119	Methylene chloride[a,b]	84
Carbon disulfide[a,b]	76	Methyl tert-butyl ether	73
Carbon tetrachloride[a,b]	117	2-Nitropropane[b]	46
Chlorobenzene[a,b]	112	Naphthalene	128
Chlorodibromomethane[a]	129	n-Propylbenzene	91
Chloroethane[a]	64	Styrene[a]	104
2-Chloroethylvinyl ether[a]	63	1,1,1,2-Tetrachloroethane	131
Chloroform[a]	83	1,1,2,2-Tetrachloroethane[a]	83
Chloromethane[a]	50	Tetrachloroethene[a,b]	164
2-Chlorotoluene	91	Tetrahydrofuran	42
4-Chlorotoluene	91	Toluene[a,b]	92
1,2-Dibromo-3-chloropropane	75	1,2,3-Trichlorobenzene	180
1,2-Dibromoethane	107	1,2,4-Trichlorobenzene	180
Dibromomethane	93	1,1,1-Trichloroethane[a,b]	97
1,2-Dichlorobenzene	146	1,1,2-Trichloroethane[a,b]	83
1,3-Dichlorobenzene	146	Trichloroethene[a,b]	95
1,4-Dichlorobenzene	146	Trichlorofluoromethane[a,b]	151
Dichlorodifluoromethane	65	1,1,2-Trichloro-1,2,2-trifluoroethane[b]	101
1,1-Dichloroethane[a]	63	1,2,3-Trichloropropane	75
1,2-Dichloroethane[a]	62	1,2,4-Trimethylbenzene	105
1,1-Dichloroethene[a]	96	1,3,5-Trimethylbenzene	105
cis-1,2-Dichloroethene[a]	96	Vinyl acetate[a]	43
trans-1,2-Dichloroethene[a]	96	Vinyl chloride[a]	62
1,2-Dichloropropane[a]	63	m,p,o-Xylenes[a,b]	106
Internal standards:		Surrogate standards:	
Pentafluorobenzene	168	Dibromofluoromethane	113
1,4-Difluorobenzene	114	1,2-Dichloroethane-d_4	65
Chlorobenzene-d_5	117	Toluene-d_8	98
1,4-Dichlorobenzene-d_4	152	4-Bromofluorobenzene	95

[a] Priority Pollutant Compounds
[b] F-list Compound

Standard Operating Procedure for Polynuclear Aromatic Hydrocarbons by HPLC

GREAT LAKES ANALYTICAL

STANDARD OPERATING PROCEDURE

FOR

POLYNUCLEAR AROMATIC HYDROCARBONS BY HPLC

GLA 8310 BG

Revision 1.1

Approved By:

Department Manager: _____ Date: _____

Quality Assurance Manager: _____ Date: 6/27/98

Laboratory Manager: _____ Date: _____

1.0 APPLICABILITY

1.1 Sample Type : This method is applicable to water, soil and waste samples.

1.2 Regulatory Applicability: Code of Federal Regulations 40

1.3 This method is used to determine the concentration of certain polynuclear aromatic hydrocarbons (PAH) in groundwater, soil and waste. Specifically, this method is used to detect the following substances:

TABLE 1

Compound	Chemical Abstract Number
Acenaphthene	83-32-9
Acenaphthylene	208-96-8
Anthracene	120-12-7
Benz(a)anthracene	56-55-3
Benzo(a)pyrene	50-32-8
Benzo(b)fluoranthene	205-99-2
Benzo(ghi)perylene	191-24-2
Benzo(k)fluoranthene	207-08-9
Chrysene	218-01-9
Dibenz(a,h)anthracene	53-70-3
Fluoranthene	206-44-0
Indeno(1,2,3,-cd)pyrene	193-39-5
1-Methyl naphthalene (Wisc.)	134-32-7
2-Methyl naphthalene (Wisc.)	91-57-6
Naphthalene	91-20-3
Phenanthrene	85-01-8
Pyrene	129-00-0

1.4. The sensitivity of this method is very dependent on the level of interferences rather than instrumental limitations. The limits of detection represent sensitivities that can be achieved in the absence of interferences. When interferences are present, the level of sensitivity will be lower. This method is used by experienced analysts or under the close supervision of qualified individuals.

2.0 SUMMARY OF METHOD

Method 8310 provides high performance liquid chromatographic (HPLC) conditions for the detection of ppb levels of certain polynuclear aromatic hydrocarbon (PAH or PNA) compounds. Prior to use of this method, appropriate sample extraction techniques are used. Samples are extracted into a solvent by sonication or separatory funnel partition. If the sample matrix is soluble in acetonitrile a waste dilution is performed. The water and soil extracts are concentrated with a Kuderna-Danish (KD).

A 10-uL aliquot of the extract is injected into an HPLC, and all compounds (except Acenaphthylene) in the effluent are detected by the fluorescence detector . Acenaphthylene is detected by the utraviolet (UV) detector.

If interference prevents proper detection of the analytes of interest, the method may also be performed on extracts that have undergone cleanup using method 3640A Gel-Permeation Chromatography (GPC).

3.0 SAFETY

It is Great Lakes Analytical's intent to provide a safe work environment for all employees. This intent is implemented in the company's Chemical Hygiene Plan (CHP). The CHP is designed to establish safe work procedures and to minimize exposure to hazardous chemicals encountered in the laboratory. The CHP is also designed to provide information to employees regarding potential hazards and training to minimize these hazards. All Material Safety Data Sheets (MSDS) are located at the Spill Response Center located in the Inorganic laboratory for review. Specific safety issues to this method are listed below:

3.1 Flammable Solvents- The flammable solvents used in this method are methanol, acetonitrile, acetone, and hexane. All flammable solvents are stored in the main warehouse area and under the extraction hoods in flammable storage cabinets. When in use, the solvents are handled in the hood at all times.

3.2 Standards- The standards used for calibrations and quality control are known pollutants; therefore caution should be taken when handling them.

3.3 Compressed Gases- Caution should be exercised when changing compressed gas cylinders. Analysts must wear safety glasses when they are changing cylinders or working with gas plumbing. Helium, nitrogen, and air are the compressed gases used in this procedure. All compressed gas cylinders must be secured to a bench, wall, or handtruck at all times. A handtruck must be used to transport cylinders The safety cap is to be in place at all times except when the cylinder is secured and a regulator is in place. All compressed gases, except air and oxygen, can cause suffocation by displacing oxygen.

3.4 Hazardous Samples- All samples that are received into the laboratory have the possibility of containing hazardous pollutants at high levels. They should be treated with caution at all times. For the management of Hazardous Samples refer to the Laboratory SOP on Hazardous Sample Management.

3.5 Fume Hoods- All extraction, sample dilutions, and standard preparations must be performed in a properly operating fume hood. All newly generated solvent waste must be stored in a container in a fume hood until it is transferred to the proper solvent waste collection container.

3.6 Gloves- Analysts performing extractions or dilutions with solvents must wear protective gloves to reduce solvent exposure through the skin. Analysts wear nitrile gloves instead of latex to help eliminate phthalate contamination to samples.

4.0 INTERFERENCES

Solvents, reagents, glassware, and other sample processing hardware may yield discrete artifacts and/or elevated baselines, causing misinterpretation of the chromatograms. All of these materials must be demonstrated to be free from interference, under the conditions of the analysis, by running method blanks. Sample extracts can become contaminated if they come in contact with contaminated glassware or syringes used in the extraction and preparation of samples with high concentrations of analytes. Glassware is thoroughly washed, deionized water rinsed, and solvent rinsed as indicated in the glassware preparation SOP. Syringes are rinsed three times with acetone, methylene chloride and acetonitrile before each use. Glassware, syringes, and dilution solvent used in waste dilution extractions are stored separately from routinely used glassware.

Interferences coextracted from the samples will vary considerably from source to source. Although a general cleanup technique is provided as part of this SOP, individual samples may require additional cleanup approaches to achieve greater sensitivity. The chromatographic conditions described allow for a unique resolution of the specific PAH compounds covered by this SOP. Other PAH compounds, in addition to matrix artifacts, may interfere. An oily matrix will have an effect on the sensitivity of the procedure as well. Oily samples are typically diluted

5.0 RECORD KEEPING

5.1 Instrument Maintenance Logbook- For each HPLC instrument, an instrument maintenance logbook is kept . It contains the instrument name, beginning date and ending date of the Logbook on the front cover. This book will include all routine instrument maintenance, repairs and any instrument modifications. All entries must be dated and initialed.

5.2 Quality Control Logbook- A quality control logbook is set up for each method of analysis. It has the method name on the outside cover. This book is divided into six parts as follows:

A. Copy of the current GLA Quality Assurance Program.

B. Copy of the appropriate methods and the GLA SOP for the analysis.

C. Copies of all calibration data.

D. Copies of all detection limit studies.

E. Copies of all retention time studies.

F. Copies of Accuracy and Precision studies.

E. Copies of all control limit studies.

5.3 Run Log- An injection logbook is setup for each instrument. Rules regarding the use of this book are as follows:

A. Each page is dated and initialed by the analyst.

B. For each sample tested documentation includes:

1. Batch number
2. Client name
3. GLA Full sample number
4. Amount of sample used
5. Matrix type
6. Dilutions made
7. Date of extraction
8. Comments

C. Laboratory notebooks must be neat and legible.

D. Mistakes are crossed out with a single line, initialed, and dated.

E. Unused pages or partial pages are Zed out.

5.4 Standards Preparation Logbook- A logbook is kept for all the standard preparations for all semivolatile methods. This book is used to record the Lot number of the stock standard solution, the compounds it includes (if it is a mix), what the standard will be used for (calibration etc.), the initial concentration of the stock solution, the dilution that is made, the final concentration, and the GLA code for the final solution. The GLA code is a special number and letter sequence used to track standards preparation within the laboratery. It consists of the month number followed by a letter of the alphabet; every month starting over with the letter A.

5.5 Reporting Results- Once analysis is completed for a group of samples and all Quality Control measures have been satisfied (see section 6) sample results can be recorded on the report worksheets. When reporting results, an analyst first checks the units on the worksheet, if they are correct he/she must circle them. Next the analyst records the date of analysis for the sample. When recording the results on the worksheet the analyst circles the compound with a positive result, and the ND is crossed out. Next to the ND, the concentration found in the sample is recorded. After an analyst has recorded the results for each sample he/she signs, and dates the first reporting page for that analysis. The analyst also records results of the spike and spike duplicate data on the QC sheet attached to the report .

5.6 LIMS Reporting- All sample results should be downloaded into the LIMS on a regular basis.

A. BATCHING- Must be done before results can be transfered to LIMS. There are several ways to batch samples. One way is to clone the extraction batch so that the analysis batch corresponds to the extraction batch:

[BATCHES]-[EDIT]-[BY BATCH]-F6

Queue = type HPLC (all caps)
Batch Rule = hit F2 , enter
Batch Queue = type EXTR (all caps)
Batch = the numerical extraction batch that is being cloned.

hit F4 twice, the extraction batch will now be given an HPLC batch number as well and the samples are ready to be transfered (posted) to LIMS.

B. DO LIST - Done in Enviroquant, this is the process of converting the data files collected to .CSV files in the C drive. This can only be done after the samples results have been batched.

hit [TOOLS]
[DO LIST]
[QUANT TO FORMS W O CALC] [OK]
Highlight the samples to be transfered and hit [ADD][PROCESS]

In order for the samples to be converted, the correct format must be used when entering sample information in the sequence including any dilution factors used. The following are examples for method 8310 water, soil, SPLP and method 610:

GLA sample # HPLC 8310WA OK
GLA sample # HPLC 8310SA OK
GLA sample #|HPLC|8310PA|OK
GLA sample#|HPLC|610 OK

C. POSTING - Transfering the .CSV files from the C drive to the LIMS drive. Can only be done at the Department Manager's terminal.

From FILE MANAGER, the files will be in C:\posted. Copy the files contained in "posted" to the HPLC LIMS drive. After the copy has been made, the files in "posted" can then be deleted.

D. PARSERING- Done in LIMS to process the .CSV files sent by POSTING.

hit [SYSTEM][PARSERS]
Program hit F2 and chose HPCHEMST
Action = type START (all caps)
Cycle = type [1]

hit F4 to commit and [ENTER] at the prompt.

6.0 QUALITY CONTROL

6.1 The GLA Quality Assurance Program must be studied and a copy is kept in each instrument's Quality Control Book.

6.2 All Method Validation requirements (see section 8) are documented in the Quality Control Book before analysis of samples can begin on an instrument.

6.3 Check Standard- Each day before analysis of samples begins the analyst verifies the calibration curve with a check standard. This standard will be from a different vendor than the calibration standard. It will be run and quantitated every 12 hours, or every 20 samples, whichever is more frequent. The analyst also evaluates the chromatography of the check standard for peak shape or coelution problems. Each day, a successful Check Standard must be analyzed before sample analyses can begin. A successful check standard contains all analytes at 85-115% recovery. Corrective action must be taken for those analytes that fall outside these limits.

6.4 Blank- No contaminants should be present in the blank above the method detection limit. If contaminants are found the blank and all related samples must be reanalyzed. If the blank contamination persists, the samples are reextracted. A blank is extracted with every batch.

6.5 Surrogates- 7,12-dimethylbenz(a)anthracene is used as the surrogate spike standard. The control limits for the surrogate are calculated using three standard deviations on either side of the average percent recovery

6.6 Accuracy and Precision- Accuracy and Precision for the method are tracked by analyzing Matrix Spike/Matrix Spike Duplicate (MS/MSD) and Blank Spike/Blank Spike Duplicate (BS/BSD) samples. The sample matrix or blank matrix is spiked with all target analytes and surrogate before extraction. The MS and MSD is analyzed every 20 samples or once a week whichever is more frequent per matrix. If there is not enough sample to extract an MS/MSD, a BS/BSD is extracted. The QC data points are tracked for each compound in each matrix (water and soil) and control limits established annually. The control limits are based on these calculations. Three standard deviations on either side of the average percent recovery serve as the control limits used to evaluate the QC.

6.7 If recoveries are not within limits, the following procedures are performed; Check to be sure there are no errors in calculations, surrogate and matrix spike solutions. Also, check instrument performance. Recalculate the data and/or reanalyze the extract if any of the above checks reveal a problem. Reextract and reanalyze the sample if none of the above are a problem or flag the data and fill out a corrective action form.

6.8 Corrective Action- Each time a quality control measure is not met, (that cannot be corrected at the instrument) a Corrective Action Report (CAR) is filled out. This report records what the problem was, how the problem was investigated , what was done to fix it, what samples were effected, and how it can be proven the problem is fixed. Corrective Action Reports are filled out whenever the blank is contaminated, MS/MSD, BS/BSD or surrogate data are out of control limits. A CAR is only used when the analyst must send the sample for re-extraction or the data must be reported with the deficiencies. The CAR is signed by the Department Manager and a copy is included with each report that requires a flag. It will then be signed by the respective Project Manager and given to the QA Manager. The original CAR is retained by the analyst.

6.9 Confirmation- The ultraviolet detector is used to confirm the presence of Polynuclear Aromatic Hydrocarbons. The GC/MS analytical technique can also be utilized for the confirmation of moderate to high levels of PAH's.

6.10 Peer Review - Peer reveiw is done on at least one batch per week. Peer review consists of a fellow analyst or supervisor looking over every aspect of the sample analysis- QC, peak identification and concentration calculation. The fellow analyst will initial and date the batch of samples reviewed.

7.0 SAMPLE MANAGEMENT

7.1 Holding Time- The Holding Time for PAH water is 7 days and soil samples is 14 days before extraction from the sampling date. In addition , there is a 40 day hold time after extraction. Most samples are stored at 4^0 C until analysis.

7.2 Disposal- All samples extracts should be kept in the refrigerator for six weeks after analysis in case further analysis is required.

8.0 METHOD PERFORMANCE

8.1 The method detection limit (MDL) is defined as "the minimum concentration of a substance that can be measured and reported with 99% confidence the reported value is not zero". This is taken from SW-846 Method 8000B . The MDLs have been determined for water and soil matrices. The MDL's are updated annually.

8.2 The precision and accuracy (P&A) for this method has been determined by preparing and analyzing blank samples for both water and soil matrices. The P&A will be updated when there is a change in HPLC analyst and with all new extractractionists.

8.3 Retention Time Study- A retention time window study is performed annually. This consists of three standards at mid-calibration concentration run over a 72 hour period. The window for analytes retention times is plus or minus three times the standard deviation of the absolute retention times. This window will be used for tentative identification of the Polynuclear Aromatic Hydrocarbons with the retention times for each compound to be updated daily.

9.0 APPARATUS AND MATERIALS

9.1 Instrumentation:

Gradient pumping system: Constant flow (Waters).

Reverse phase column HPLC conditions: Reverse phase VYDAC reverse phase C18, 5 micron particle size, in a 250-mm x 4.6-mm I.D. stainless steel column

Detectors: Fluorescence (Waters 470) and UV detectors (Waters 486) are used. UV detector: 254-nm, coupled to the fluorescence detector.

Personal Computer: A data system for measuring peak areas and retention times using Enviroquant software.

10.0 REAGENTS

10.1 Reagent water: Reagent water is defined as water in which an interference is not observed at the method detection limit of the compounds of interest (PAHs).

10.2 Acetonitrile: HPLC quality, distilled in glass.

10.3 Stock standard solutions:

10.3.1 Commercially prepared stock standards are purchased from various suppliers. Two different sets of standards are used for this analysis. One standard is used for spiking of samples (MS/MSD) and blanks (BS/BSD) and have all analytes at the same concentration levels. The other standards used for instrument calibration contain the PAHs at varying concentrations. The daily check standard is prepared from a different source than the initial calibration standards.

10.3.2 The stock standards are transferred into Teflon-sealed screw-cap vials. The standards are stored at 4° C and protected from light. Stock standards are checked for signs of degradation, or evaporation.

10.3.3 Stock standard solutions are replaced after one year, or sooner if comparison with check standard indicates a problem.

10.4 Calibration standards: Calibration standards at a minimum of five (typically greater than five) concentration levels are prepared through dilution of the stock standards with acetonitrile. One of the standards is at a concentration near, but above, the instrument detection limit. The remaining concentration levels should correspond to the expected range of concentrations found in real samples or should define the working range of the HPLC. The calibration standard must be replaced after six months, or sooner if comparison with check standards indicated a problem.

10.5 Calibration standards preparation: Calibration standards are made up of four ampules combined to calibrate all eighteen compounds and the surrogate. The first ampule contains a PNA mix which contains all compounds except 1-Methylnaphthalene, 2-Methylnaphthalene and the surrogate. The other three ampules are for each of the three remaining compounds.
The typical concentrations found in the ampules are as follows:

PNA mix	2000 ug/mL
7,12-dimethylbenz(A)anthracene	1000 ug/mL
1-Methylnaphthalene	1000 ug/mL
2-Methylnaphthalene	1000 ug/mL

To prepare a 50 mL aliquot of a 10,000 ug L solution, add 500 uL of 7,12-dimethylbenz(A)anthracene, 1-Methylnaphthalene and 2-Methylnaphthalene. Add 250 uL of the PNA mix and bring up to volume with Acetonitrile. Use this 10,000 ug L stock solution to prepare a set of standards which range from 5.0 ppb to 7,000 ppb and using the 10,000 ppb stock solution as the final standard.

10.6 Internal standards (if internal standard calibration is used): Internal standards are not used in this method.

10.7 Surrogate standards: This analysis is monitored for the performance of the extraction, cleanup (if necessary), analytical system, and the effectiveness of the method in dealing with each sample matrix by spiking each sample, standard, and reagent blank with one, two, or three surrogates recommended to encompass the range of the temperature program used in this method. Currently GLA uses 7,12-dimethylbenz(a)anthracene as the surrogate.

11.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

11.1 Sample Preservation- Samples are stored at 4 C prior to extraction. No additional preservation is needed.

11.2 Sample extracts must be stored under refrigeration and the extracts must be analyzed within forty days of the extraction date.

12.0 PROCEDURE

analyst plans the sequence enters the sample numbers into the sequence file, and record all the needed information into the Run Log. The ence will be as follows:

A Check Standard (contains all compounds with each RF ·· =15% difference from initial calibration)
B Acetonitrile Blank
C Samples or QC samples (# of samples/QC based on 12 hour clock)
D Check Standard
E Repeat steps C and D

12.2 The Calibration Check Standard is quantitated and all QC criteria must be met before analysis of samples can begin. All reportable samples and spikes must be bracketed by good Check Standards. Any samples not bracketed must be reanalyzed

12.3 Sample Introduction: All samples are introduced into the chromatographic system using an autosampler.

12.4 If all the QC requirements for the day have been met, the samples have been shot at the proper dilution, and the hits have been analyzed the results are ready for peer review.

12.5 Peer review is done on at least one batch per week. Peer review consists of a fellow analyst or supervisor looking over every aspect of the sample analysis- QC, peak identification and concentration calculation The fellow analyst will initial and date the batch of samples reviewed.

12.6 Once the peer review is completed the samples from the batch can be reported (see section 5.5).

12.7 HPLC analysis: What follows is the sequence of events necessary to clean, equilibrate and start the instrument analysis.

12.7.1. Morning Maintenance:

a. Check Helium tank pressure.
b. Check Compressed Air Tank pressure.
c. Fill Acetonitrile reservoir.
d. Fill water reservoir.
e. De-gas newly filled solvents for approximately 15 minutes.
f. Fill needle wash bottles with Acetonitrile.
g. Dispose of solvent waste in Flammable Solvent Waste drums.
h. Remove Check Standard and all samples to be run from the refrigerator and allow to come to room temperature.

12.7.2. Running Samples:

a. Operate Gradient Function -
Necessary to prepare the instrument for the initial conditions to run the samples.

On the Gradient controller, press [OPERATE GRADIENT] [8][ENTER][ENTER][2][ENTER].
The instrument should run without sample injection at this setting for approximately 5 minutes.

b. Create the Sequence-

Necessary to collect and retrieve data from samples that have run.

In the GCTop-

hit SEQUENCE-SAVE

enter the date you want the data saved under.

hit EDIT SEQUENCE LOG

enter the amount of samples that will run with the appropriate method and individual sample information. Hit [MORE] to enter additional information such as sample dilutions and printing options (select "NONE" as a printing option so the sample information will not print during the run). When all information has been entered hit [OK].

hit [LOAD AND RUN SEQUENCE]

enter [OK] at the prompts. choose and enter correct date.

When prompt reads "READY TO INJECT" you can begin running.

c. Starting the run on the WISP-

This will inject the samples and begin the run.

1. Open the door and place samples in the carousel.

2. While door is still open press [SYS MES][7][7][ENTER] then the last sample number in the carousel [ENTER].

3. Close the door press [RUN/STOP], the red light will move from STOP to RUN.

4. To pause WISP during a run just open door, this will prevent the next sample from being injected.

12.7.3. Generating the report-

The report consists of the sample results and the corresponding chromatogram

a. LOAD DATA FILE - bring up the file to be quantitated . The samples run on LC-1 will be found in C: hpchem\5 data date run. The samples run on LC-2 will be found in C: hpchem\6\data\ date run.

b. UPDATE RETENTION TIMES - Update the retention time of the first check standard run before that sample. To do this hit [TOOLS] [EASYID] ; underline each peak for the appropriate compound. After updating and saving all peak changes, hit [FILE][SAVE METHOD] to save to the method. Quantitate all samples run after the check standard with that check standards retention times. When subsequent check standard appears, repeat the above procedure.

c. QUANTITATE RESULTS- After updating the proper check standard retention times, pull up the sample file you wish to quantitate. Be sure the correct method is loaded and then hit [CALCULATE AND GENERATE REPORT]. If any compounds required manual integration, hit [QUANT][Q EDIT QUANT RESULT]. Every attempt should be made to avoid the use of manual integration. If absolutely necessary, it must be performed in a manner which is consistent with the integration of the standards used for calibration. The manipulation of integration parameters in a way that is inconsistent with the integration of the calibration standards constitutes fraud, and is strictly forbidden.

d. PRINT RESULTS - To print results that have been quantitated, hit [TOOLS][DO LIST][SUMMARY QUANT W/OUT CALCULATIONS] and highlight those you want printed. This will print the quantitated results with any Qedit changes made.

e. CALCULATIONS- Dividing factors necessary to convert report results (instrument report values in ppb) to reportable units. These calculations assume a starting volume of 1 liter of sample for waters and 30 grams of sample for soil samples.

Illinois Waters in mg/L :	Result / 100,00
Wisconsin Waters in ug/L:	Result / 100
Illinois Soils in mg/kg:	Result / 3,000
Wisconsin Soils in ug/kg :	(Result / 3)*Dry Weight

If the volume weight is less than the assumed starting value, then a dilution factor is applied to the above calculations and the reporting limit, equal to the inverse of the percentage used.

For example, if an soil is extracted with a starting weight of only 15 grams , then as defined above, the dilution factor equal to the inverse of of the percentage used or 15 grams 30 grams = 0.50 ; 1 0.50 = 2. The dilution factor of 2 will then be applied to both the applicable calculation and the reporting limit.

13.0 MAINTENANCE AND TROUBLESHOOTING

13.1 Isolate the Problem

When troubleshooting any system the first and most difficult step is to isolate the problem before fixing it. This is accomplished by following the path of analysis either forward or backwards and eliminating properly functioning parts of the system. This is done until the problem can be isolated to one area or part. The instruments in the system give error messages when there is an electrical or software problem. For this type of situation the analyst should refer to the Instrument Manual's troubleshooting section. The analyst should follow the direction in the manual or call technical support to try to resolve the problem. At this point outside help may be needed to replace a defective part. All symptoms of problems should be documented in the insrument Log to facilitate troubleshooting .

13.2 Routine Maintenance

To prevent breakdown and contamination problems the System should be maintained routinely.

13.3 Trouble Shooting

13.3.1 Broad Peaks or Poor Peaks Resolution - Change guard column.

13.3.2 High pressure - Change guard column
Prime pump

13.3.3 No or low pressure - Check for leaks

13.3.4 Noisy baseline - Check source

13.3.5 No peaks - check the Gradient Program

13.3.6 Increased Retention Time - Flow rate decreasing ; check for leaks.

13.3.7 Upon opening door of WISP tray will not release - Check air tank.

14.0 REFERENCES

1. Testing Methods for the Evaluating of Solid Waste. Physical/Chemical Methods. SW-846. 3RD Edition, Methods 3510B. 3550B. and 8310.

2 "Determination of Polynuclear Aromatic Hydrocarbons in Industrial and Municipal Wastewaters." EPA-600/4-82-025. US. Environmental Monitoring and Support Laboratory. Cincinnati. Ohio 45268. September 1982.

3 "EPA Method Validation Study 20. Method 610 (Polynuclear Aromatic Hydrocarbons)." Report for EPA Contract 68-03-2624.

4 U.S. EPA 40 CFR Part 136. "Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act: Final Rule and Interim Final Rule and Proposed Rule." October 26. 1984.

5 Provost. L.P. and R.S. Elder. "Interpretation of Percent Recovery Data" American Laboratory. 15. pp. 58-63. 1983.

6. GLA Quality Assurance Program. Version 5.7.

7. GLA Chemical Hygiene Plan, Version 2.2.